tion of certain 2,2′-bipyridine[19] and ethylene-diamine[20] metal complexes were likewise observed to be acid catalyzed. Finally it is of interest to note that the rate of alcoholysis of benzyl fluoride is acid catalyzed but that of other benzyl halides is not;[10] this is analogous to the behavior of the haloamminecobalt(III) complex ions.

The rate of loss of optical activity of an aqueous solution of d-cis-[Coen$_2$F$_2$]$^+$ at a pH of 1 shows clearly that this proceeds in two distinct steps (Fig. 1). There is first a change in optical rotation followed then by a slower loss of optical activity. Within rather large limits of experimental error, the initial mutarotation proceeds at approximately the same rate as does the hydrolysis under these same conditions (Table IV). This suggests that d-cis-[Coen$_2$F$_2$]$^+$ is converted to d-cis-[Coen$_2$H$_2$OF]$^{2+}$ without extensive loss in optical rotation. The fluoroaquo product in turn undergoes racemization at a rate independent of the rate of release of the second fluoride. No detailed kinetic study was made of the hydrolysis of the second fluoride except to observe that it was very slow compared to the rate of loss of optical activity.

TABLE IV

RATES OF ACID HYDROLYSIS, MUTAROTATION AND RACE-MIZATION OF d-cis-[Coen$_2$F$_2$]$^+$ GIVEN IN $k(min.^{-1})$.

[HNO$_3$]	Temp., °C.	Acid hydrolysis	Mutaro-tation	Racemiza-tion
no acid	25	1.8×10^{-4}	...	...
0.001	25	3.6×10^{-4}	4.9×10^{-4}	$\sim 2 \times 10^{-4}$
0.1	25	3×10^{-3a}	6.2×10^{-3}	3.9×10^{-4}
0.1	35	1×10^{-2a}	1.3×10^{-2}	4.7×10^{-4}

^{a} The method of removal of complex on an ion exchange resin prior to titration of fluoride was employed. Because of difficulties described in experimental these data are only semi-quantitative.

This change in optical rotation of an acid solu-

(19) J. H. Baxendale and P. George, Trans. Faraday Soc., 46, 736 (1950); F. Basolo, J. C. Hayes and H. M. Neumann, This Journal, 75, 5102 (1953).

(20) J. Bjerrum, K. G. Paulsen and I. Paulsen, "Symposium on Co-ordination Chemistry," Danish Chemical Society, 51 (1953).

tion of d-cis-[Coen$_2$F$_2$]$^+$ is analogous to the behavior which Mathieu[21] reports for l-cis-[Coen$_2$Cl$_2$]$^+$. He suggests that since the rate of racemization of d-cis-[Coen$_2$H$_2$OCl]$^{2+}$ is not dependent on the rate of replacement of the chloro group, it must involve a dissociation of the coördinated water to yield a symmetrical intermediate. Recently[22] it was shown that the loss of optical activity is primarily due to isomerization to the symmetrical $trans$-[Coen$_2$H$_2$OCl]$^{2+}$ which can in turn regenerate the racemic cis isomer. Tentatively it can also be concluded that the racemization of d-cis-[Coen$_2$H$_2$OF]$^{2+}$ likewise proceeds by an exchange of coördinated water with the solvent. Before more definite statements can be made, it must be determined whether or not the rate of water exchange is sufficiently rapid to permit such a mechanism. One final point of interest is that the rates of racemization for a series of complex ions of the type [Coen$_2$H$_2$OX] decrease with changes of X in the order Cl$^-$> F$^-$> NO$_2^-$~ NCS$^-$>> NH$_3$. If all that is involved in racemization is the water exchange, then it is surprising that the chloro-aquo complex racemizes approximately 200 times faster than does the nitroaquo whereas the rate of acid hydrolysis of cis-[Coen$_2$Cl$_2$]$^+$ is only twice that of cis-[Coen$_2$NO$_2$Cl]$^+$. This can be understood if the replacement of water in the nitroaquo complex takes place a larger percentage of the time without loss of optical activity as compared to the chloro-aquo compound. This is in agreement with the π-bonding hypothesis[1] which predicts that the contribution of π-bonding electrons from chloride to cobalt in the pentacoördinated intermediate, [en$_2$Co=Cl]$^{2+}$, enhances the formation of a trigonal bipyramid structure whereas the tetragonal pyramid structure is favored for [en$_2$Co-NO$_2$]$^{2+}$ which does not have this type of π-bonding.

(21) J. P. Mathieu, Bull. soc. chim., [5] 4, 687 (1937).

(22) R. G. Pearson, R. E. Meeker and F. Basolo, This Journal, 78, 2673 (1956).

EVANSTON, ILL.

The Mechanism of the Formation and Rearrangement of Nitritocobalt(III) Ammines[1]

By R. Kent Murmann[2] and Henry Taube[3]

The formation of a group of nitritocobalt(III) ammines from the aquo complexes proceeds in weakly acidic solutions without breaking the cobalt-oxygen bond. The formation of the nitro derivative from nitritopentammine-cobalt (III) ion proceeds in water solution by an intramolecular process involving either the formation of a pentacoördinated intermediate followed by instantaneous reaction with the group released or via a heptacoördinated activated state.

I. Introduction

The rate of substitution of a ligand for another on cobalt(III) and chromium(III) coördination compounds is often quite slow. Certain ions, however, substitute more rapidly and a correlation has been made.

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between the nucleophilic character of these reactants and the rate and mechanism of the reaction has been made.[4] A consideration of the literature values of the rates of substitution reactions reveals a group which seem to proceed more rapidly than one would anticipate on this basis. Comparison of the following rates indicates that the fast group consists of the reaction between an aquo-coördination compound and a labile-oxygen containing
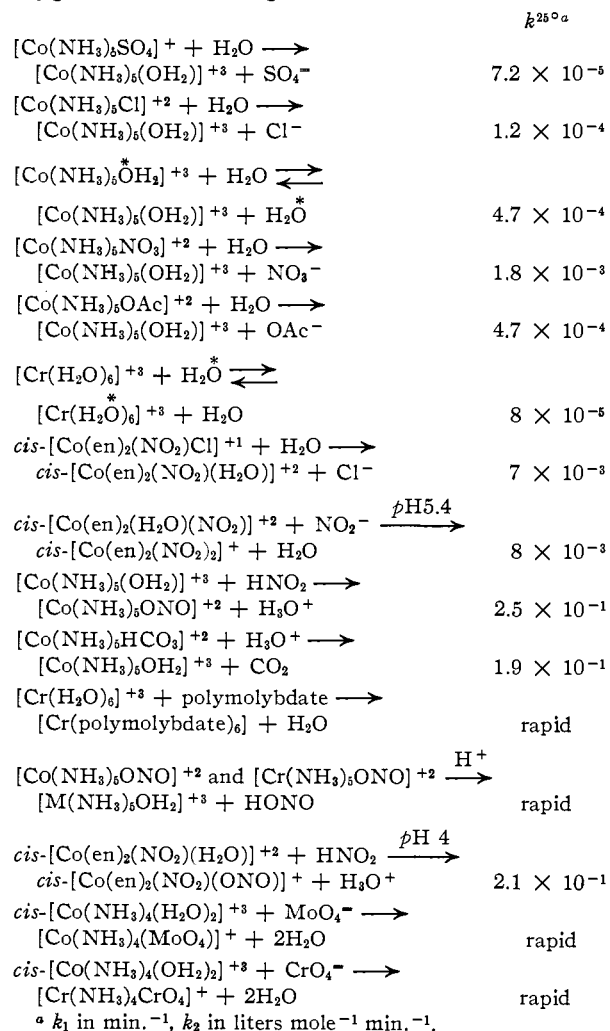
(4) D. D. Brown and C. K. Ingold, J. Chem. Soc., 2680 (1953).

ion. Thus there is a plausible explanation for the abnormal speeds in the possibility of the cobalt–oxygen bond remaining intact.

$k^{25°a}$

[Co(NH$_3$)$_5$SO$_4$]$^+$ + H$_2$O ⟶
    [Co(NH$_3$)$_5$(OH$_2$)]$^{+3}$ + SO$_4^-$ 7.2×10^{-5}

[Co(NH$_3$)$_5$Cl]$^{+2}$ + H$_2$O ⟶
    [Co(NH$_3$)$_5$(OH$_2$)]$^{+3}$ + Cl$^-$ 1.2×10^{-4}

[Co(NH$_3$)$_5$ÖH$_2$]$^{+3}$ + H$_2$O ⇌
    [Co(NH$_3$)$_5$(OH$_2$)]$^{+3}$ + H$_2$Ö 4.7×10^{-4}

[Co(NH$_3$)$_5$NO$_3$]$^{+2}$ + H$_2$O ⟶
    [Co(NH$_3$)$_5$(OH$_2$)]$^{+3}$ + NO$_3^-$ 1.8×10^{-3}

[Co(NH$_3$)$_5$OAc]$^{+2}$ + H$_2$O ⟶
    [Co(NH$_3$)$_5$(OH$_2$)]$^{+3}$ + OAc$^-$ 4.7×10^{-4}

[Cr(H$_2$O)$_6$]$^{+3}$ + H$_2$Ö ⇌
    [Cr(H$_2$Ö)$_6$]$^{+3}$ + H$_2$O 8×10^{-5}

cis-[Co(en)$_2$(NO$_2$)Cl]$^{+1}$ + H$_2$O ⟶
    cis-[Co(en)$_2$(NO$_2$)(H$_2$O)]$^{+2}$ + Cl$^-$ 7×10^{-3}

cis-[Co(en)$_2$(H$_2$O)(NO$_2$)]$^{+2}$ + NO$_2^-$ $\xrightarrow{pH5.4}$
    cis-[Co(en)$_2$(NO$_2$)$_2$]$^+$ + H$_2$O 8×10^{-3}

[Co(NH$_3$)$_5$(OH$_2$)]$^{+3}$ + HNO$_2$ ⟶
    [Co(NH$_3$)$_5$ONO]$^{+2}$ + H$_3$O$^+$ 2.5×10^{-1}

[Co(NH$_3$)$_5$HCO$_3$]$^{+2}$ + H$_3$O$^+$ ⟶
    [Co(NH$_3$)$_5$OH$_2$]$^{+3}$ + CO$_2$ 1.9×10^{-1}

[Cr(H$_2$O)$_6$]$^{+3}$ + polymolybdate ⟶
    [Cr(polymolybdate)$_6$] + H$_2$O   rapid

[Co(NH$_3$)$_5$ONO]$^{+2}$ and [Cr(NH$_3$)$_5$ONO]$^{+2}$ $\xrightarrow{H^+}$
    [M(NH$_3$)$_5$OH$_2$]$^{+3}$ + HONO   rapid

cis-[Co(en)$_2$(NO$_2$)(H$_2$O)]$^{+2}$ + HNO$_2$ $\xrightarrow{pH\ 4}$
    cis-[Co(en)$_2$(NO$_2$)(ONO)]$^+$ + H$_3$O$^+$ 2.1×10^{-1}

cis-[Co(NH$_3$)$_4$(H$_2$O)$_2$]$^{+3}$ + MoO$_4^-$ ⟶
    [Co(NH$_3$)$_4$(MoO$_4$)]$^+$ + 2H$_2$O   rapid

cis-[Co(NH$_3$)$_4$(OH$_2$)$_2$]$^{+3}$ + CrO$_4^-$ ⟶
    [Cr(NH$_3$)$_4$CrO$_4$]$^+$ + 2H$_2$O   rapid

^{a} k_1 in min.$^{-1}$, k_2 in liters mole^{-1} min.$^{-1}$.

Isotope studies on the acid decomposition of [Co(NH$_3$)$_5$CO$_3$]$^+$ have shown that it is the carbon–oxygen bond which is broken while the oxygen originally attached to the cobalt remains attached in aquo ion.[5] The acid decomposition of [Co-(NH$_3$)$_4$CO$_3$]$^{+1}$, however, results in one of the two cobalt oxygen bonds being broken.[6]

It has been reported[7] that the formation of [Co(NH$_3$)$_5$ONO]$^{+2}$ from the aquo salt proceeds in slightly acid medium according to the following rate law

rate = k([Co(NH$_3$)$_5$OH]$^{+2}$)(HNO$_2$)^2

The interpretation is that N$_2$O$_3$ (NO$^+$NO$_2^-$) attacks an unshared pair of oxygen electrons forming the nitrito compound and releasing H$^+$NO$_2^-$. It was suggested that if this were the mechanism, then the cobalt–oxygen bond would not be broken.

The rearrangement of nitrito compounds to the nitro form proceeds either in the anhydrous solid

(5) J. P. Hunt, A. C. Rutenberg and H. Taube, THIS JOURNAL, 74, 268 (1952).

(6) F. Posey and H. Taube, ibid., 75, 4099 (1953).

(7) R. G. Pearson, P. M. Henry, J. G. Bergman and F. Basolo, ibid., 76, 5920 (1954).

state or in solution. It has been postulated[7,8] that this is an intramolecular reaction on the basis of the solid state reaction and the rate in solution being essentially independent of the nitrite ion concentration.

This paper reports the results obtained using O^{18} as a tracer, to elucidate the mechanism of the formation of nitrito compounds of Co(III) and Cr-(III) ammines and of the nitrito–nitro conversion.

II. Experimental

A. Preparation of Compounds.—The starting materials [Co(NH$_3$)$_5$(OH$_2$)](ClO$_4$)$_3$-H$_2$O,[9] cis-[Co(en)$_2$(NH$_3$)Cl]-(NO$_3$)$_2$,[10] cis-[Co(en)$_2$(NO$_2$)Cl](NO$_3$),[11] cis-[Co(NH$_3$)$_4$-(OH$_2$)$_2$]Cl$_3$,[12] cis-[Co(en)$_2$(NO$_2$)$_2$]NO$_3$,[13] [Cr(NH$_3$)$_5$Cl]Cl$_2$,[14] [Co(NH$_3$)$_5$(NO$_2$)](ClO$_4$)$_2$[15] and cis-[Co(en)$_2$Cl$_2$]Cl[16] were prepared according to procedures in the literature. They were recrystallized twice and dried under vacuum.

Aquo compounds enriched in O^{18} were prepared in two ways: (1) equilibration of the normal aquo salt with acidified enriched water for 48 hr. at 50°, in the dark, followed by precipitation with sodium perchlorate or bromide; (2) triturating the pure chloro compound in enriched water with 0.2% less than the equivalent amount of AgNO$_3$ or AgClO$_4$ at 5° and removing the silver halide on a filter. The filtrates which gave no test for silver ion and only a faint test for halide ion, were evaporated to dryness under vacuum at 20°. The crystals were washed with alcohol and dried or, if an oil was obtained, it was solidified by repeated extraction with absolute alcohol. The chromium compounds were protected from light to prevent decomposition. It is known that there is little cis-trans conversion in these reactions.[17]

The nitrito compounds were prepared by the addition of an excess of sodium nitrite to a saturated water solution of the aquo complex at 5°. Perchloric acid was added until a pH of about 4 was reached and after 10 minutes the crystalline product collected on a filter. (In cases of cis-bis-(ethylenediamine)–amminenitritocobalt(III) and cis-tetramminedinitrito–cobalt(III) ions it was necessary to add an excess of sodium bromide to obtain a product.) The nitrito compounds were washed with 95% ethanol to remove the adhering sodium nitrite, recrystallized by solution in the minimum amount of water at 5° and addition of a cold saturated solution of sodium perchlorate or bromide. The crystals were repeatedly washed with cold alcohol, then with acetone and dried under vacuum at 10°. Recrystallization was absolutely necessary in order to remove the last traces of NO$_2^-$ which, if present, seriously interfere with the determination of the O^{18}-content of the compounds. Since the nitrito compounds are unstable with respect to the nitro form, they were stored at approximately 0° and in all cases were used within an hour of their preparation.

Anal. Calcd. for [Co(NH$_3$)$_5$ONO](ClO$_4$)$_2$: Co, 15.14; N, 21.62; H, 3.88. Found: Co, 15.21; N, 21.46; H, 3.69. Calcd. for cis-[Co(en)$_2$(NH$_3$)(ONO)]Br$_2$: Co, 14.65; N, 20.92; Br, 39.8. Found: Co, 14.59; N, 20.76; Br, 39.6. Calcd. for cis-[Co(en)$_2$(NO$_2$)(ONO)](ClO$_4$): Co, 15.90; C, 12.95; H, 4.35; N, 22.70. Found: Co, 15.80; C, 13.08; H, 4.39; N, 22.58. Calcd. for [Cr(NH$_3$)$_5$-ONO]Br$_2$: N, 24.52; Br, 46.6. Found: N, 24.29; Br, 46.3. Calcd. for [Co(en)$_2$(ONO)$_2$]ClO$_4$: Co, 15.92; N, 22.70. Found: Co, 15.78; N, 22.79.

Isotopically labeled nitrito compounds of the type (R$_5$-Co-Ö-N-Ö) were prepared from the enriched aquo compound by treatment with an aged, acidic, enriched water solution of enriched NaNO$_2$. Separation and purification were the same as for the unenriched samples except that enriched water was used for recrystallization. Complete ex-

(8) B. Adell, Svensk. Kem. Tids., 56, 318 (1944).

(9) F. Ephraim, Ber., 56, 1936 (1923).

(10) S. M. Jorgensen, J. prakt. Chem., [2] 41, 454 (1890).

(11) A. Werner, Lieb. Ann., 386, 248 (1912).

(12) S. M. Jorgensen, Z. anorg. Chem., 2, 294 (1892).

(13) A. Werner and E. Humphrey, Ber., 34, 1821 (1901).

(14) O. T. Christensen, J. prakt. Chem., 23, 54 (1881).

(15) F. Ephraim, Ber., 56, 1532, 1540 (1923).

(16) A. Werner, ibid., 44, 875 (1911).

(17) A. Werner, Ber., 44, 2445 (1911).

change of the nitrite ion with water was assumed and fractionation effects were small enough to be neglected.

Sodium nitrite, enriched in O^{18}, was prepared by mixing known amounts of $NaNO_2$ of normal isotopic composition with a large amount of enriched H_2O and acidifying the solution to a pH of 4.5 with 70% perchloric acid. After 3 hours at room temperature the exchange was complete and Na_2-HPO_4 (anhydrous) was added to a pH of about 7. The water was removed under vacuum. The presence of sodium phosphate does not interfere with the preparation of the nitrito complexes.

All common chemicals were of reagent grade and were purified by crystallization where necessary.

B. Isotopic Determination.—In order to obtain a gaseous sample representative of the O^{18}-content of the nitrito complexes, which could be introduced into the mass spectrometer, thermal decomposition of the complexes was carried out. Unfortunately a mixture of oxides of nitrogen was obtained which could not conveniently be used.

The O^{18}-content of N_2O can be measured conveniently and accurately in the mass spectrometer, and has the advantages of being relatively inert and condensable allowing its separation from CO_2, N_2 and O_2. Thus the nitrito complexes reacted to give NO_2^- which was converted to N_2O which had the same oxygen isotopic composition as the average of the two oxygens of the nitrito compound. It has been shown that N_2O exchanges with the solvent very slowly[18a] and the observation that NO_2^- exchanges at high pH's has been described.[18b] The latter exchange has never been noted even in the presence of a large excess of azide ion. It would appear that the inorganic complex is very successful in preventing this exchange.

Three methods were used to obtain NO_2^- from nitrito compounds.

Method A.—The action of 0.1 N NaOH at about 40° for 1 hour yielded NO_2^- and either the corresponding hydroxy complex or at higher temperatures degradation products including $Co(OH)_3$ and NH_3. This reaction takes place with about 90% fission of the Co–O bond and about 10% N–O breaking. The relative contribution of the two reactions is not easily controlled and thus this method gave poor precision.

Method B.—Reaction of the nitrito complex with methoxide ion (perhaps partially hydroxide ion because of the difficulty in obtaining alcohol in an absolutely anhydrous state) in absolute methanol results in NO_2^- whose oxygens have the exact O^{18}-composition of the original coördination compound. A small pellet of pure, dry, sodium was placed in the bottom of a Urey tube and the dry nitrito complex placed inside of the hollow bore stopcock. The vessel was evacuated and pure methanol (dried over BaO) was distilled over the sodium and frozen with liquid N_2. On warming, methoxide ions were formed while the H_2 was removed by evacuation. The Urey tube was tipped to allow the complex to drop into the reacting solution and after one hour at 50° the mixture was distilled to dryness under vacuum. The NO_2^- formed was converted to N_2O by reaction with NaN_3 under buffered conditions.

Method C.—All known cobalt coördination compounds containing the nitrito group rearrange in the solid state to the nitro form. The dry nitrito compounds were heated at 50° for 6 hr. to effect this conversion and the resulting nitro compound treated for 2 hr. with an excess of 0.1 N NaOH at 50°. Nitrite ion was released and either the hydroxy compound or decomposition products resulted. The mole fraction of O^{18} in the NO_2^- was identical with the average of those in the nitrito complex.

Since NO_2^- exchanges with H_2O only at low pH's[18b] the conversion to N_2O should be carried out under neutral or alkaline conditions. The experiments with neutral hydrazine produced little N_2O (mostly N_2) and some exchange occurred. Best results were obtained with buffered NaN_3 solution. The exchange of NO_2^- with H_2O is extremely sensitive to pH while the rate of reaction of N_3^- with NO_2^- is less so. In each case raising the H^+ concentration increases the rate of reaction. It was shown that N_2O could be formed without exchange if the pH was carefully controlled and if regions of high acidity were avoided during addition of reagents. This procedure was carefully followed, the order of addition, pH and the temperature being most im-

portant, but even with great care occasional samples showed anomalous exchange. Two milliliters of a solution containing the NO_2^- to be analyzed was placed into one side of a two-compartment reaction vessel and into the other 3 ml. of sodium phosphate buffer (pH 3.9).[19] The vessel was immersed in a $CO_2(s)$-methanol mixture and about 0.1 g. of solid NaN_3 placed on top of the frozen buffer solution. While still frozen, the vessel was evacuated, closed off from the vacuum system, and the NO_2^- compartment warmed. Immediately on melting of a portion of the NO_2^- solution, the vessel was tipped so as to pour it on the frozen NaN_3-buffer mixture. Rapid mixing was accomplished and the solution warmed to 40° for 15 min. Isolation of the crude N_2O was carried out by freezing the mixture with liquid N_2 and removing the N_2 and O_2 by evacuation. The N_2O was transferred to a tube containing NaOH pellets and it was shaken five minutes to remove CO_2 and HN_3 and transferred to another vessel for isotopic analysis. In the conversion of NO_2^- to N_2O there is less than 1% exchange with the solvent.

When method B was used to prepare NO_2^-, a modified procedure was necessary. To the evacuated vessel containing the dried sample a 1.0 M solution of NaN_3 was introduced through the stopcock without the admission of air. Following this, the cold buffer solution was added slowly in the same manner with agitation. After 15 min. at 40° the isolation and purification were carried out in the usual manner.

The mole fraction of O^{18} present in enriched $NaNO_2$ was determined by conversion to N_2O and measurement of the mass ratio 46 (44 + 46). The experimental value agreed reasonably well with that calculated from the relative amounts of normal $NaNO_2$ and enriched H_2O used in its preparation. In the case of $[Co(NH_3)_5(OH_2)](ClO_4)_3$, the O^{18}-enrichment was determined by precipitation of the complex as the bromide, removal of the water by heat, equilibration of known amounts of the H_2O and CO_2, and measurement of the isotopic ratio in the CO_2.[20] The results obtained in this manner agreed with that calculated on the basis of the relative amounts of the starting materials assuming complete exchange. For all other aquo compounds the isotopic ratio was calculated from the known isotopic composition of the starting materials and the relative amounts used. The concentration of O^{18} in the enriched water was determined by accurate dilution with normal water, equilibration with CO_2 and mass spectrometer analysis.

The mass $46/(44 + 46)$ ratio of the N_2O was measured in a Consolidated Nier Isotope mass spectrometer. All samples were compared with a standard N_2O sample prepared with normal reagents and were normalized to a value of 2.00×10^{-3} for the standard.

C. Rate of Exchange.—The rate of exchange of NO_2^- with $[Co(NH_3)_5NO_2](ClO_4)_2$ was conducted at 27.0° in 0.1 N buffer solutions at pH 5.45 and 6.35. The concentration of the labeled coördination compound (twice recrystallized from methanol-water solution. *Anal.* Calcd. for [Co-$(NH_3)_5NO_2](ClO_4)_2$: N, 21.62. Found: N, 21.52) was 2.5×10^{-3} M/l. and of normal $NaNO_2$, 5.0×10^{-3} M/l. The solutions were protected from light and no decomposition was detected by measurement of the extinction coefficient at 460 mμ. The nitro complex was separated by addition of excess $NaBr(s)$ and purified by solution in water and precipitation with $NaBr(s)$. Recrystallization was necessary since preliminary experiments indicated some $NaNO_2$ was carried down with the solid. The pure complex was washed with alcohol and acetone and dried *in vacuo*. Conversion to N_2O was carried out by method C.

D. Mutarotation of cis-$[Co(en)_2(NO_2)(ONO)]ClO_4$.—The preparation and resolution of this compound has been previously described.[21] The rate of mutarotation was followed at 19° in pure water while the rate of conversion to the nitro form was carried out spectrophotometrically under the same conditions at 440 mμ.

III. Results and Discussion

Since $[Co(NH_3)_5OH_2]^{+3}$, (ROH_2), exchanges its water with the solvent slowly at room temperature,

(18) (a) A. Bothner-By and L. Friedman, *J. Chem. Phys.*, **20**, 4591 (1952); (b) M. Anbar and H. Taube, THIS JOURNAL, **76**, 6244 (1954).

(19) The buffer was prepared by mixing equal volumes of concentrated H_3PO_4 and H_2O and neutralizing it with concentrated NaOH until a pH of 3.9 was obtained. Since the ionic strength and the Na$^+$ concentration was high the pH has only qualitative significance.

(20) M. Cohn and H. C. Urey, THIS JOURNAL, **60**, 679 (1938).

(21) R. Kent Murmann, *ibid.*, **77**, 5190 (1955).

the preparation of O^{18}-enriched $[Co(NH_3)_5ONO]^{+2}$, (RONO), from normal H_2O, NO_2^- and enriched (ROH_2) was thought possible if, during the reaction, the cobalt–oxygen bond is not broken. Preliminary determinations produced a small enrichment in the (RONO) which could not be explained without a partial retention of the cobalt–oxygen bond. Further work showed that exchange with the solvent was occurring during the conversion of (RONO) to N_2O. Refined techniques reduced this exchange to a negligible amount permitting exact determinations on the mechanism to be carried out.

Table I shows a portion of the results on the conversion of NO_2^-. Using hydrazine as the reactant at pH 2 or 8 resulted in appreciable exchange. The high value of $R_N(H_2O)$ in experiments 1–3 results from the enriched water used in the preparation of $\overset{*}{N}O_2^-$. In later work this water was removed. Experiment 7 was carried out with an enriched, equilibrated NO_2^-–H_2O solution and buffer of approximately the same O^{18} mole fraction. The N_2O value in experiment 8 with the same $\overset{*}{N}O_2^-$, converted in normal water and buffer, when compared with number 7, shows that little exchange occurs in this formation of N_2O from NO_2^-.

TABLE I

FORMATION OF N_2O FROM NO_2^-

No.	$R_N \times 10^3$ (NO_2^-)	$R_N \times 10^3$ (H_2O)	Method	$R_N \times 10^3$ (N_2O)	Exchanges, %
1	8.43	2.81^a	NH_2NH_2 pH 2	2.99	97
2	8.43	2.81^a	NH_2NH_2 pH 8	3.48	88
3	8.43	2.81^a	N_3^-, buffer, pH 3.8	8.40	0.5
4	4.29	2.00	N_3^-, buffer, pH 3.8	4.24	2.0
5	9.65	2.00	N_3^-, buffer, pH 3.8	9.52	1.5
6	12.02	2.00	N_3^-, buffer, pH 3.8	12.08	−0.6
7	13.92	13.92	N_3^-, buffer, pH 3.8^b	13.92^c	.0
8	13.92	2.00	N_3^-, buffer, pH 3.8	13.88 ± 0.12^c	.4

^{a} Solvent from NO_2^- enrichment not removed. ^{b} Buffer solution enriched; $R_N = 13.5$. ^{c} Average of five determinations.

Several methods of converting (RONO) to NO_2^- were tried before non-exchange of oxygen was obtained. Table II contains these experiments carried out with $(R\overset{*}{O}N\overset{*}{O})$ and with salt prepared from $(R\overset{*}{O}H_2)$, and NO_2^- in dilute acid solution. The

TABLE II

FORMATION OF NO_2^- FROM $[Co(NH_3)_5ONO](ClO_4)_2$

No.	$R_N \times 10^3$ (H_2O)^b	Method	$R_N \times 10^3$ (N_2O)	% Breaking Co–O Bond
		$[Co(NH_3)_5(\overset{*}{O}N\overset{*}{O})]^{+2a}$		
9	14.02	A	14.00	...
10	1.99	A	13.91^d	98.4
11	1.99	NaN_3, pH 8	9.63	27.1
12	1.99	C	13.99 ± 0.08^c	99.8
		$[Co(NH_3)_5(\overset{*}{O}NO)]^{+2e}$		
13	14.02	A	7.89	...
14	1.99	A	7.74	97.7
15	1.99	B	7.88	100.0
16	1.99	C	7.86^c	99.8
17	1.99	NH_2NH_2-pH 8	3.92	32.8

^{a} $R_N \times 10^3 = 14.00$–14.02. ^{b} Solvent. ^{c} Average for four determinations. ^{d} Highest value obtained. Average value 13.49–8.5% O–N breaking. ^{e} $R_N \times 10^3 = 13.76$–1.99.

reaction was allowed to proceed for no more than 4 min. at 5–8° to reduce the amount of exchange of the solvent with the aquo complex. Since $t_{1/2}$ for these exchanges are in the range 5–30 hr. at 25° very little replacement of O^{18} by O^{16} occurs. The nitrito complexes were recrystallized in cold normal water, washed with alcohol to remove the nitro compound and dried. Experiments 12, 15, 16 show that methods B and C are good methods of converting RONO to NO_2^- while experiments 10 and 14 indicate that alkaline substitution is primarily on the cobalt oxygen. Therefore 14–16 show that the compound made from $R\overset{*}{O}H_2$ and NO_2^- retains the Co–O bond intact.

Table III confirms these conclusions and extends them to other cations. The values listed are the highest obtained but are probably lower limits.

TABLE III

FORMATION OF R-ONO FROM $ROH_2{}^a$

$R_N \times 10^3$ $[Co(NH_3)_5OH_2]^{+3}$	$R_N \times 10^3$ (NO_2^- and H_2O)	Method	$R_N \times 10^3$ (N_2O)	% Retention of Co–O Bond
14.00 (14.06)^c	1.99^b	B	7.96	99.4
9.86^c	1.99^b	B	5.86	98.3
13.94^c	1.99^b	C	7.93	99.4
1.99^b	13.87^d (13.99)^c	C	7.97^e	99.3

Compound	$R_N \times 10^3$ (Complex)^c	$R_N \times 10^3$ (NO_2^- and H_2O)^b	Method	$R_N \times 10^3$ (N_2O)	% Retention of Co–O Bond
cis-$[Co(NH_3)_4(OH_2)_2]^{+3}$	8.43	1.99	C	4.96	92.3
cis-$[Co(en)_2(NO_2)(OH_2)]^{+2}$	8.62	1.99	C	5.28	99.5
cis-$[Co(en)_2(NH_3)(OH_2)]^{+3}$	8.95	1.99	C	5.22	93.0
$[Cr(NH_3)_5OH_2]^{+3}$	5.62	1.99	B	3.43	79.5
cis-$[Co(en)_2(OH_2)_2]^{+3}$	8.22	1.99	C	5.02	97.5

^{a} Reaction time 3 min., temp. 5–6°. ^{b} Determined by equilibration with CO_2. ^{c} Value calculated from composition of equilibration mixture. ^{d} Determined by conversion to N_2O. ^{e} Average value of three determinations.

The experimental results clearly show, as was concluded by Basolo and Pearson,[7] substitution on the complex ion oxygen in the nitrosation of some aquo coördination compounds. The identity of the nitrosating agent is not clear but in solutions containing large amounts of NO_2^- it probably is $(N\overset{+}{O}N\bar{O}_2)$. It is of interest to point out that anhydrous $N\overset{+}{O}Cl$ does not react with $[Co(NH_3)_5-OH_2](ClO_4)_3$ after one hour at −5° but this does not preclude the possibility of its participation in solutions high in Cl^-.

The change in mechanism under slightly alkaline conditions is noteworthy. The formation of the nitro complex is relatively slow and does not involve the nitrito intermediate. The reaction probably proceeds by two paths, the most important being dissociation followed by entry of a nitrite ion while displacement is less favorable.

This type of substitution is probably not limited to the formation of nitrito compounds. For, if dissociation and displacement are slow, a labile oxygen containing ion may rapidly replace the labile hydrogen of a complex ion and form the product. The rate of exchange of oxyanions is often quite sensitive to environment and thus (in the nitrito system) raising the pH or changing to a less polar solvent leads to a much slower reaction which does not involve the nitrito intermediate. The

reaction of MoO_4^- or WO_4^- with cis-[Co(en)₂-(H₂O)₂]+³ differs from the NO_2^- example in that it is rapid even under neutral or slightly alkaline conditions.[22a] Unlike NO_2^- both of these oxyions undergo rapid exchange with water in this pH range.[22b] It is suggested that these ions may also react by substitution on the cobalt oxygen.

In order to study the conversion of (RONO) to the (RNO₂) form, it was necessary to demonstrate the non-exchange of NO_2^- with (RNO₂). This was carried out at 27° in the dark by determining the O¹⁸-content of NO_2^- and (RN̊O₂) in a solution containing these ions in a molar ratio of 2 to 1. Less than 2% exchange was observed after 50 hr. at a pH of 5.45 and 6.35. Table IV contains the

TABLE IV

CONVERSION OF [Co(NH₃)₅(ONO)]+² TO [Co(NH₃)₅(NO₂)]+²

| $R_N \times 10^3$ [Co(NH₃)₅· ONO]+²	$R_N \times 10^3$ (H₂O)	$R_N \times 10^4$ (N₂O)	Conditions^a	Ex-change, %
1.99-1.99	14.06	1.99	pH 6.3, 60°, 0.5 hr.	0.0
1.99-1.99	13.99	2.00	pH 5.0, 60°, 0.5 hr.	.1
13.19-1.99	..	7.59	Solid, 60°, 1 hr.	..
13.19-1.99	1.99	7.60	pH 5.5, 60°, 0.5 hr.	.0
13.19-1.99^b	1.99	7.54	pH 6.0, 0.5/1 ratio NO₂⁻ to complex, 25°, 12 hr.	.7
1.99-11.41	..	6.70	Solid, 60°, 1 hr.	..
1.99-11.41	1.99	6.65	pH 6.0, 60°, 0.5 hr.	1.0
1.99-11.41^b	1.99	6.69	pH 5.0, 5/1 ratio NO₂⁻ to complex, 14 hr. at rm. temp.	0.2

^a Carried out in water solution unless otherwise noted. ^b Carried out in the presence of NO_2^-; $R_N(NO_2^-) = 2.00 \times 10^{-3}$.

evidence for an intramolecular rearrangement. Neither the cobalt oxygen nor the oxygen attached only to the nitrogen exchanges with the solvent or with added NO_2^- during the transformation. Preliminary results with cis-[Co(en)₂(NO₂)(ON-O)]+ also show negligible exchange during rearrangement even in the presence of NO_2^-. Thus, in at least two cases [Co(NH₃)₅ONO]+² and cis-[Co(en)₂(NO₂)(ONO)]+, the rearrangement is certainly an intramolecular one as concluded by Adell[23] and by Basolo and Pearson.[7] Furthermore, optically active cis-[Co(en)₂(NO₂)(ONO)]+ mutarotates at the same rate as the nitrito–

(22) (a) R. Kent Murmann, unpublished results; (b) N. F. Hall and O. R. Alexander, THIS JOURNAL, 62, 3455 (1940); G. A. Mills, ibid., 62, 2833 (1940).

(23) B. Adell, Svensk. Kem. Tids., 56, 318 (1944); 57, 260 (1945); Acta Chem. Scand., 5, 941 (1951).

nitro conversion and ultimately leads to the active dinitro complex without racemization or inversion.[21] It is suggested that if the –ONO group is released, it must immediately attach its nitrogen before it leaves the sphere of influence of the complex. This is essentially identical with a heptacoördinated activated state.
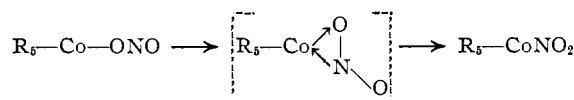
The rate of rearrangement of [Co(NH₃)₅ONO]+² in acid solutions has been measured by Adell.[23] No decomposition but a decreased rate compared to neutral solutions was observed. We have observed the same phenomenon but find that at the higher acid concentrations (0.07 N) nitrogen bubbled through the solution removes traces of either oxides of nitrogen or nitrous acid while small quantities of the aquo compound are formed. We interpret this in terms of an equilibrium involving the aquo complex. Since the rate of water exchange of [Co(NH₃)₅OH₂]+³ is essentially independent of [H+] and [SO₄⁻][24] it would seem that direct replacement by NO_2^- is not a probable mechanism. Thus it is suggested that the lowered rate of formation of [Co(NH₃)₅NO₂]+² in slightly acid solutions is due to an equilibrium which removes a portion of the nitrito complex: the reaction going to completion by a shift of the equilibrium concentrations on depletion of the nitrito complex.

$$[R_5CoOH_2] + HONO \xrightleftharpoons{\ H^+, (H_2O)\ } [R_5Co\text{-}ONO] \longrightarrow [R_5CoNO_2]$$
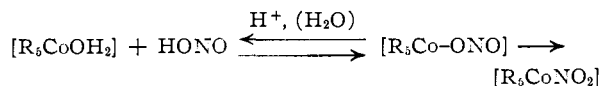
The constitution of the nitrosating agent in the absence of excess NO_2^- has not been elucidated. The anion catalysis parallels that observed in the aquation of [Co(NH₃)₅SO₄]+ [25] and in the exchange of [Cr(H₂O)₆]+³ [26] with water which may indicate a strong ion pair effect.

We wish to express our appreciation to Howard Baldwin for some of the isotope ratio measurements.

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