# 350. *Tracer Studies in the Aquation and Hydrolysis of Cobalt Complexes.*

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Heavy oxygen being used as an isotopic tracer, it has been shown that in the hydrolysis of *C*-substituted acetatopentamminocobalt(III) ions $[R\cdot CO_2\cdot Co(NH_3)_5]^{++}$ there is a gradual change of the position of bond fission in the series R = $CH_3$, $CH_2Cl$, $CCl_3$, $CF_3$ from the Co–O bond with the weakly acidic acetic acid ligand to the C–O bond with the strongly acidic trifluoroacetic acid ligand. In aquation of acetato- and of trifluoroacetato-pentamminocobalt(III) ions there is no evidence for the breaking of the C–O bond. Evidence is put forward to suggest that the aquation of carbonatopentamminocobalt(III) nitrate may be regarded as a decarboxylation giving two products of normal abundance.

In an investigation of the mechanism of substitution reactions in complex ions, Basolo, Bergmann, and Pearson (*J. Phys. Chem.*, 1952, **56**, 22) made a kinetic study of the hydrolysis and aquation of two series of *C*-substituted acetatopentamminocobalt(III) ions, one containing carboxylate groups of different base strength, and the other containing carboxylate groups of analogous base strength but of different size. The rates were found to parallel the base strength of the co-ordinated ligand but not its size, and these electronic and steric effects were taken as evidence that the substitution occurred either by an ionization mechanism or by a mechanism of the $S_N2$ type. As in certain cases it was found that the rate of hydrolysis was of second order, indicating a bimolecular mechanism, it was suggested that both hydrolysis and aquation involved nucleophilic substitution at the cobalt atom, with the entering groups approaching from the opposite side to the displaced carboxyl group.

This reasoning, however, gives no proof of the point of bond fission in either hydrolysis or aquation. In the aquation of carbonatopentamminocobalt(III) nitrate, Hunt, Rutenberg, and Taube (*J. Amer. Chem. Soc.*, 1952, **74**, 268) have shown by tracer studies that the Co–O bond is not broken, and suggest by analogy that similar bond fission may also occur in replacement reactions of carboxylatopentamminocobalt(III) complexes. It was decided to investigate the position of bond fission in hydrolysis and aquation of various carboxylatopentamminocobalt(III) complexes by $^{18}O$ tracer technique. For hydrolysis the acetato-, and monochloro-, trichloro-, and trifluoro-acetato-, and for aquation, the acetato- and trifluoroacetato-complexes were studied. The reactions involved in hydrolysis and aquation may be written

$$[Co(NH_3)_5X]^{++} + OH^- \longrightarrow [Co(NH_3)_5OH]^{++} + X^-$$
$$[Co(NH_3)_5X]^{++} + H_2O \longrightarrow [Co(NH_3)_5,H_2O]^{+++} + X^-$$

It was not possible to follow the tracer in the substituting groups $OH^-$ and $H_2O$ because of the subsequent exchange of the $^{18}O$ in the hydroxy- or aquo-complex with the solvent, and it was decided to make the isotopic analysis on the carboxylic acid.

Two general methods of isolation of the carboxylic acid after reaction were used. In the first, the carboxylic acid was extracted with ether, from a slightly acid solution, and converted into the silver or sodium salt, which was decomposed to carbon dioxide by heating it *in vacuo* or in an atmosphere of bromine respectively. This general method was applied to the separation of the acid produced by hydrolysis of the acetato- and mono- and tri-chloroacetato-complexes and by the aquation of the acetato-complex.

In the second general method the hydroxy- or aquo-complex was removed from the reaction mixture by absorption on alumina, and the resulting neutral solution evaporated *in vacuo* and the dried sodium salt decomposed by bromine as before. This method was applied to the products of the hydrolysis of monochloro-, trichloro-, and trifluoro-acetato-complexes and the aquation of the last complex. It was found that the aquation of both acetato- and trifluoroacetato-complexes gave fission of the Co–O bond, and that hydrolysis of acetato- and mono- and tri-chloro-acetato-complexes gave completely or largely fission of the Co–O bond, but that hydrolysis of trifluoroacetato-complex gave fission of the C–O bond. In the aquation of carbonatopentamminocobalt(III) nitrate the isotopic composition of the carbon dioxide evolved was measured and found to be very nearly normal.

## EXPERIMENTAL

The *C*-substituted acetatopentamminocobalt(III) nitrates were prepared according to the method of Basolo, Bergmann, and Pearson (*loc. cit.*) from the carbonatopentamminocobalt(III) nitrate (Werner and Gosling, *Ber.*, 1903, **36**, 2380; Lamb and Mysels, *J. Amer. Chem. Soc.*, 1945, **67**, 468) and analysed for ammonia by Horan and Eppig's method (*ibid.*, 1949, **71**, 581).

*General Procedure for Hydrolysis.*—A few hydrolyses were carried out under the conditions used by Basolo, Bergmann, and Pearson (*loc. cit.*) but in general the solutions used by these investigators were too dilute for convenient analysis and the following procedure was adopted.

Enriched water (20 ml.) was made 0·2N by addition of sodium hydroxide and 0·2M in the cobalt complex. The mixture was shaken until solution was complete and kept at 25° for 1—5 hr. depending on the nature of the complex.

*Methods of Isolation.—Ether-extraction.* The reaction mixture was filtered from any small precipitate of cobalt hydroxide, and brought to pH 1 by addition of nitric acid (5N), and the carboxylic acid extracted four times with ether. From each extraction the ether was run into sodium hydroxide solution (5N) to convert the free acid into the sodium salt in the aqueous layer. This separated aqueous layer was neutralised with nitric acid, barium chloride (50 mg.) added, and the solution filtered from any barium carbonate. The solution was evaporated to dryness *in vacuo*, and the residue warmed in bromine vapour. The permanent gas was pumped off at −180°, then the reaction mixture was allowed to warm to −80°, and the carbon dioxide examined by mass-spectrometer.

With the acetato-complex, silver nitrate was sometimes added to the neutralized reaction mixture at pH 5, and the precipitated silver acetate dried and decomposed by heat.

*Alumina-extraction.* The reaction mixture was filtered and allowed to percolate slowly through a dry column of alumina. The emerging liquid was a colourless neutral solution of the sodium salt of the carboxylic acid. Barium chloride (50 mg.) was added, and the solution filtered from carbonate. The solvent was distilled off *in vacuo*, and the residue treated with bromine as previously described.

These methods of extraction were checked by a number of experiments in which both normal and isotopically enriched samples of the acid were isolated under typical conditions.

*General Procedure for Aquation.*—Enriched water (20 ml.) was made 0·2M in the cobalt complex, brought to pH 4 by addition of nitric acid, and kept at 65° for 1—4 hr., depending on the nature of the complex. The reaction mixture was then brought to pH 1 and subjected to the ether-extraction method of isolation, or made alkaline with sodium hydroxide, and the carboxylic acid isolated by the alumina method.

*Results.*—It was first shown that the methods of decomposition of the salts of the carboxylic acids to carbon dioxide gave carbon dioxide of an isotopic abundance sufficiently close to that of a sample of cylinder gas for the latter value to be used as a standard normal value of the isotopic composition in all our experiments. The values quoted for isotopic abundances of $^{18}O$ (Table 1) were determined by comparing the relative abundances of masses 44 and 46, *i.e.*, $^{12}C^{16}O^{16}O$ and $^{12}C^{16}O^{18}O$. The contribution to 46 by the species $^{13}C^{16}O^{17}O$ was ignored. If

TABLE 1. *Tests of isolation and decomposition methods.**

| Acid | | Abundance of $^{18}O$ in solvent $H_2O$, atoms-% excess | Method of isolation | Salt | Abundance of $^{18}O$, atoms-% excess |
|---|---|---|---|---|---|
| Hydrolysis conditions. | | | | | |
| Enriched ......... | $CH_3\cdot CO_2H$ | Normal | $Et_2O$ extn. | Ag * | 0·465 |
| | | | ,, | Na | 0·438 |
| Enriched ......... | $CH_2Cl\cdot CO_2H$ | Normal | Direct | Na | 0·703 |
| | | Normal | $Al_2O_3$ | Na | 0·738 |
| Normal ............ | $CH_2Cl\cdot CO_2H$ | 1·29 | ,, | Na | 0·026 |
| | | 1·29 | ,, | Na | 0·036 |
| | | 1·45 | $Et_2O$ extn. | Na | 0·010 |
| Enriched ......... | $CCl_3\cdot CO_2H$ | Normal | Direct | Na | 1·298 |
| | | Normal | $Et_2O$ extn. | Na | 1·260 |
| Enriched ......... | $CCl_3\cdot CO_2OH$ | Normal | Direct | Na | 0·633 |
| | | Normal | $Al_2O_3$ | Na | 0·623 |
| Enriched ......... | $CCl_3\cdot CO_2H$ | Normal | Direct | Na * | 0·319 |
| | | Normal | $Al_2O_3$ | Na | 0·310 |
| Normal ............ | $CCl_3\cdot CO_2H$ | 1·45 | $Et_2O$ extn. | Na | 0·032 |
| | | 1·12 | $Al_2O_3$ | Na | 0·030 |
| | | 1·12 | ,, | Na | 0·060 |
| Enriched ......... | $CF_3\cdot CO_2H$ | Normal | Direct | Na | 1·138 |
| | | Normal | $Al_2O_3$ | Na | 1·120 |
| Normal ............ | $CF_3\cdot CO_2H$ | 0·74 | ,, | Na | 0·084 |
| Aquation conditions. | | | | | |
| Normal ............ | $CF_3\cdot CO_2H$ | 1·36 | Direct | Na | 0·315 |
| | | 1·36 | $Al_2O_3$ | Na | 0·278 |
| | | 1·36 | ,, | Na | 0·293 |

* The method of decomposition was by bromination, except that in the two cases thus marked it was by heat.

TABLE 2.

| Complex | Abundance of $^{18}O$ in solvent $H_2O$, atom-% excess | Time of reaction, hours | Abundance of $^{18}O$ in $CO_2H$ group | Atoms-% from water |
|---|---|---|---|---|
| | *Hydrolysis results.* | | | |
| $[Co(NH_3)_5,CH_3\cdot CO_2](NO_3)_2$ ......... | 1·12 | 5 | 0·050 | 4 |
| | 1·12 | 5 | 0·038 | 3 |
| | 1·12 | 5 | 0·064 | 6 |
| | 1·12 | 5 | 0·021 | 2 |
| $[Co(NH_3)_5,CH_2Cl\cdot CO_2](NO_3)_2$ ...... | 1·45 | 3 | 0·09 | 6 |
| | 1·29 | 5 | 0·12 | 9 |
| | 0·97 | 3 | 0·07 | 7 |
| $[Co(NH_3)_5,CCl_3\cdot CO_2](NO_3)_2$ ......... | 1·450 | 1 | 0·167 | 12 |
| | 0·696 | 24 * | 0·143 | 20 |
| | 0·696 | 6 * | 0·170 | 24 |
| | 0·740 | 1 | 0·114 | 16 |
| | 0·740 | 1 | 0·087 | 13 |
| $[Co(NH_3)_5,CF_3\cdot CO_2](NO_3)_2$ ......... | 0·696 | 24 * | 0·345 | 50 |
| | 0·696 | 6 * | 0·321 | 46 |
| | 0·740 | 1 | 0·396 | 53 |
| | 0·740 | 1 | 0·422 | 57 |
| | 0·740 | 1 | 0·394 | 53 |
| | 0·740 | 1 | 0·413 | 56 |
| | *Aquation results.* | | | |
| $[Co(NH_3)_5,CH_3\cdot CO_2](NO_3)_2$ ......... | 1·53 | 4 | 0·065 | 4 |
| | 1·53 | 4 | 0·030 | 2 |
| $[Co(NH_3)_5,CF_3\cdot CO_2](NO_3)_2$ ......... | 1·36 | 2 | 0·393 | — |
| | 1·36 | 2 | 0·224 | — |

* Indicates reaction carried out under Basolo, Bergmann, and Pearson's kinetic conditions.

(abundance of mass 44)/(abundance of mass 46) = $R$, we have total atoms % of $^{18}O = 100/(2R + 1)$ = atoms-% excess + atoms-% in normal gas.

*Tests of Isolation of Carboxylic Acids.*—In these experiments the carboxylic acids of normal and enriched isotopic abundance were dissolved in water (normal and enriched) and kept under reaction conditions for an appropriate time. The acids were then isolated and decomposed to carbon dioxide by either of our general methods (see Tables 1 and 2).

*Carbonato-aquation.*—Carbonatopentamminocobalt(III) nitrate (0·1 g.) was dissolved in enriched water (5 c.c.) at 0° and degassed. Concentrated hydrochloric acid (3 drops) was added *in vacuo*, and after a few min. the mixture was cooled to $-80°$ and the abundance of $^{18}O$ in the evolved carbon dioxide was measured (see following table). In the last experiment the reaction mixture was kept at room temperature for 40 min.

| | | | | | |
|---|---|---|---|---|---|
| Abundance of $^{18}O$ in solvent $H_2O$, atoms % excess | 1·36 | 1·36 | 1·36 | 1·36 | 1·36 |
| Atoms, %, of $^{18}O$ in $CO_2$ .................................. | 0·021 | 0·075 | 0·022 | 0·052 | 0·136 |
| Atoms, %, from $H_2O$ .................................... | 1·5 | 5 | 1·5 | 4 | 10 |

The methods of isolation and decomposition were also tested in a few cases by using enriched acids of known abundance.

## DISCUSSION

The tracer experiments in the aquation of acetato- and trifluoroacetato-pentamminocobalt(III) nitrate give no evidence for the breaking of the C–O bond The appreciable abundance of $^{18}O$ in the trifluoroacetic acid isolated from aquation is probably due to the extraneous oxygen exchange between this acid and water, which can occur, as shown by blank experiments, in the acidic solutions used for aquation.

It seems therefore that aquation of these carboxylato-complexes of cobalt(III) involves either an ionization mechanism or a bimolecular attack of a solvent molecule on the cobalt, *i.e.*, by $S_N1$ or $S_N2$ reactions, respectively. Neither the kinetic measurements of Basolo, Bergmann, and Pearson (*loc. cit.*) nor the tracer experiments reported here differentiate between these two possible mechanisms. The absence of acid catalysis under the conditions of the kinetic measurements as shown by Basolo, Bergmann, and Pearson indicates that the reacting entity is $[Co(NH_3)_5,R\cdot CO_2]^{++}$ and the reactions can be written as

$$(S_N1)\quad [Co(NH_3)_5,R\cdot CO_2]^{++} \longrightarrow [Co(NH_3)_5]^{+++} + R\cdot CO\cdot O^- \longrightarrow [Co(NH_3)_5,H_2O]^{+++}$$

$$(S_N2)\quad H_2O + [Co(NH_3)_5,R\cdot CO_2]^{++} \longrightarrow [(H_2O)Co(NH_3)_5]^{+++} + R\cdot CO\cdot O^-$$

In the hydrolysis of the carboxylato-complexes of pentamminocobalt(III) there appears to be a gradual change of the position of bond fission from the Co–O bond in the weakly acidic acetic acid ligand to the C–O bond in the strongly acid trifluoroacetic acid ligand. Both reactions are shown by their kinetic forms to be bimolecular and are therefore comparable to the $S_N2$ and $B_{AC}2$ mechanisms, respectively, of substitution and of ester hydrolysis (Day and Ingold, *Trans. Faraday Soc.*, 1941, **37** 686; Bunton, Hughes, Ingold, and Meigh, *Nature*, 1950, **166**, 679):

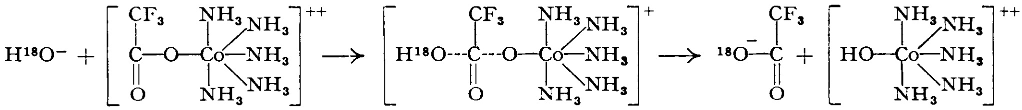
$$(S_N2)\quad {}^{18}OH^- + [Co(NH_3)_5\text{-}\vdots\text{-}O\cdot CO\cdot CH_3]^{++} \longrightarrow [H^{18}O\text{–}Co(NH_3)_5]^{++} + CH_3\cdot CO\cdot O^-$$

$$(B_{AC}2)\quad {}^{18}OH^- + [Co(NH_3)_5\text{–}O\text{-}\vdots\text{-}CO\cdot CF_3]^{++} \longrightarrow [Co(NH_3)_5OH]^{++} + CF_3\cdot CO\cdot {}^{18}O^-$$

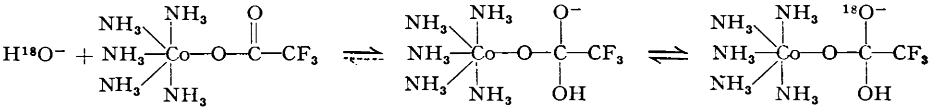
The $B_{AC}2$ mechanism is strongly favoured by electron withdrawal from the carbonyl-carbon atom, facilitating nucleophilic attack on this atom, and it is observable in the trichloroacetato-complex despite probable steric hindrance by the three chlorine atoms to attack on the carbonyl-carbon atom. In the hydrolysis of the trifluoroacetato-complex the very powerful electron withdrawal by the three fluorine atoms and the absence of steric hindrance makes the $B_{AC}2$ mechanism of prime importance.

It is not possible to ascertain from tracer experiments in their present form the precise amount of carbon-oxygen fission in any experiment.

If the $B_{AC}2$ mechanism involves a single-stage bimolecular substitution on the carbonyl-carbon atom, one of the two atoms of the isolated acid will be derived from the water, and the isotopic abundance of the acid will therefore be 50% of that of the water :



The mechanism may, however, involve the formation of a carbonyl-addition intermediate of finite life as observed in the hydrolysis of carboxylic esters (Bender, *J. Amer. Chem. Soc.*, 1951, **73**, 1626):



In this case some oxygen from the water will appear in the unhydrolysed cobalt complex, and the isotopic abundance of the isolated acid will therefore be more, by a small amount, than 50% of that of the water.

The uncertainty in our isotopic results owing to the small extraneous enrichment which occurs during isolation is such that we cannot differentiate between the two possibilities for the $B_{AC}2$ mechanism.

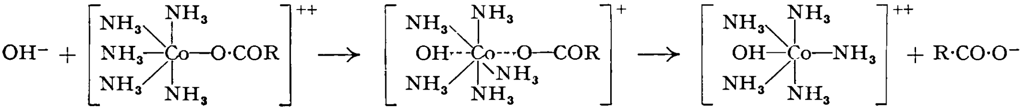
The tracer evidence for a change of bond fission, together with Basolo, Bergmann, and Pearson's kinetic measurements (*loc. cit.*), gives the following relative rate sequences for the two mechanisms:

Cobalt–oxygen bond fission, $S_N2$ : $CH_3{\cdot}CO_2 < CH_2Cl{\cdot}CO_2 < CCl_3{\cdot}CO_2 > CF_3{\cdot}CO_2$.

Carbon–oxygen bond fission, $B_{AC}2$ : $CH_2Cl{\cdot}CO_2 < CCl_3{\cdot}CO_2 < CF_3{\cdot}CO_2$.

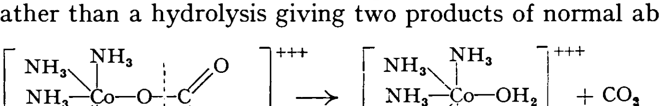
This rate sequence suggests an increased facility of attack on the cobalt on passage from acetato- to trichloroacetato-, with a marked decrease from trichloro- to trifluoro-acetato-; this decrease may be due to hydrogen bonding between the fluorine atoms and the hydrogen atoms of the ammino-groups. Such hydrogen bonding would inhibit nucleophilic attack on the cobalt atom. The electrostatic nature of the hydrogen bonding will probably increase the electron density on the cobalt atom and therefore inhibit the attack of hydroxide ion at this centre.

The hydrogen bonding could also make it more difficult for the five ammino-groups to take up their position in the transition state of the bimolecular displacement mechanism



Similar hydrogen bonding has already been suggested as a probable explanation of the formation of stable un-ionized addition compounds between trifluoroacetic acid and ethers and tertiary amines; this is in direct contrast to the inertness of acetic acid under similar conditions.

In the aquation of the carbonatopentamminocobalt(III) complex which reacts in solution as the bicarbonate complex (Lamb and Mysels, *J. Amer. Chem. Soc.*, 1945, **67**, 468) we find that the carbon dioxide evolved is of approximately normal isotopic abundance and that the small amount of tracer in the carbon dioxide is simply due to partial equilibration with the water. This evidence, taken in conjunction with Hunt, Rutenberg, and Taube's conclusion (*ibid.*, 1952, **74**, 268) that the cobalt–oxygen bond is not broken, a result which we have confirmed, shows that aquation of the carbonato-complex is a decarboxylation, rather than a hydrolysis giving two products of normal abundance:



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