*Inorganica Chimica Acta*, 37 (1979) 67–70

# Acetato Complexes of Pentaamminecobalt(III). The Kinetics and Mechanism of the Titanium(III) Reduction

R. MARČEC and M. ORHANOVIĆ

*Institute 'Rudjer Bošković', Zagreb, Croatia, Yugoslavia*

Received March 6, 1979

*The kinetics of the reduction of acetato-, trichloroacetato-, and trifluoroacetatopentaamminecobalt(III) complexes by titanium(III) in acidic aqueous chloride media have been studied at 25 °C and* $\mu$ = *1.0* M *(*$H^+$, $Na^+$, $Cl^-$*)* [1]. *At hydrogen ion concentration between 0.2 and 0.01* M *the rate law is of the form* $-d\ln[Co(III)] = k_{-1}[H^+]^{-1}[Ti(III)]$ *with* $k_{-1} \doteq (4.9 \pm 0.3) \times 10^{-3}\ s^{-1}$, $(1.8 \pm 0.2) \times 10^{-5}\ s^{-1}$, *and* $(1.6 \pm 0.2) \times 10^{-5}\ s^{-1}$ *for the acetato-, trichloroacetato, and trifluoroacetato- complex. Comparisons with reductions by the usual reducing agents is made and it is concluded that* $TiOH^{2+}$ *reduces the trifluoroacetato- and trichloroacetato-complex in an outer sphere mode while reduction of the acetato-complex occurs by an inner sphere mechanism. The change in the mechanism within this series of similar ligands is discussed.*

## Introduction

It has been shown that Ti(III), like Cr(II), Cu(I), V(II), and Eu(II) undergoes inner sphere oxidation by a variety of carboxylatocobalt(III) complexes [2–4]. In fact, an inner sphere mechanism has been proposed for all mononuclear Co(III)-carboxylato complexes thus far studied [2, 3]. Substitution reactions on titanium(III) center are believed to occur by an associative mechanism, which seems to extend also to the 2+ charged $TiOH^{2+}$ species [5–7]. If so, then inner sphere reductions by $TiOH^{2+}$ might prove to be more sensitive to the nucleophilicity of the bridging ligand than are inner sphere reductions by Cr(II), Cu(I), V(II), and Fe(II). In this work we report a kinetic study on the Ti(III) reduction of acetato-, trichloroacetato-, and trifluoroacetatopentaamminecobalt(III) complex ions.

## Experimental

### *Materials*

The perchlorate salts of $Co(NH_3)_5(OOCCH_3)^{2+}$, $Co(NH_3)_5(OOCCCl_3)^{2+}$, and $Co(NH_3)_5(OOCCF_3)^{2+}$ were prepared according to the literature procedure [8, 9]. Perchlorate anion was replaced by chloride using a Sephadex SP-C-25 ion exchange column. The Co(III) complexes were charged onto the column, washed with acidic 0.05 *M* NaCl and eluted with acidic 0.2 *M* NaCl. Purity of the complexes in solutions so obtained was ascertained by their visible–UV spectra which agreed with those reported. The solutions were stored in the dark at 0 °C, where they were stable for an extended period of time, in agreement with the slow aquation rates of the complexes [10].

Titanium(III) solutions in aqueous chloride medium were prepared, analyzed, and handled as previously described [11]. Other materials were of the same brand and purity as used in the previous study [12].

### *Kinetic Measurements*

The kinetics were followed spectrophotometrically. Decreases of the absorbance were measured at 502 nm for all the three Co(III) complexes and additionally at 349 nm for $Co(NH_3)_5(OOCCCl_3)^{2+}$ and $Co(NH_3)_5(OOCCF_3)^{2+}$. A Cary 17 instrument was used. The fitting of the instrument and the technique applied was similar to that previously reported [11]. Conditions for pseudo first order kinetics were established by the use of at least 18 fold excess of titanium(III) over cobalt(III) concentration. Pseudo first order rate constants were determined from the slopes of the standard linearized plots. The reduction rates of $Co(NH_3)_5(OOCCCl_3)^{2+}$ and $Co(NH_3)_5(OOCCF_3)^{2+}$ were very slow and most of the kinetics were followed only for a 20–25% extent of the reaction. The 'infinity' absorbance readings in these cases were obtained from blank spectra of the products assumed on the basis of the 1:1 stoichiometry and a fast dissociation of the corresponding Co(II) products. The 'infinity' absorption spectra taken after completion of the $Co(NH_3)_5(OOCCH_3)^{2+}$ + Ti(III) kinetic runs agreed with this assumption.

All the runs were performed at 25 °C in chloride anionic medium and at 1.0 *M* ionic strength adjusted by HCl and NaCl.

TABLE I. Rate Constants for the Oxidation of Titanium(III) by $Co(NH_3)_5L^{2+}$ Ions at 25 °C and $\mu$ = 1.0 *M* (HCl + NaCl).

| L | $[H^+]$/m*M* | [Ti(III)]/m*M* | $10^4$ $k_{obsd}/s^{-1}$ | $10^3$ $k_{II}/M^{-1}$ $s^{-1}$ [a] | |
|---|---|---|---|---|---|
| | | | | exp. | calc. |
| Acetato[b] | 198 | 11.8 | 2.5 | 21 | 25 |
| | 100 | 11.8 | 5.3 | 45 | 49 |
| | 52.9 | 8.88 | 8.1 | 92 | 92 |
| | 38.9 | 3.48 | 3.9 | 110 | 130 |
| | 25.9 | 11.2 | 26 | 230 | 190 |
| | 20.1 | 8.90 | 25 | 290 | 240 |
| | 14.7 | 8.36 | 35 | 420 | 330 |
| | 11.2 | 3.62 | 17 | 480 | 440 |
| | 10.2 | 7.70 | 37 | 460 | 480 |
| | 1000 | 59.0 | 2.4 | 4.1[e] | |
| Trichloroacetato[c] | 202 | 69.7 | 0.058 | 0.080 | 0.090 |
| | 103 | 69.7 | 0.15 | 0.22 | 0.17 |
| | 47.1 | 33.3 | 0.10 | 0.29 | 0.38 |
| | 33.3 | 44.5 | 0.26 | 0.60 | 0.50 |
| | 20.5 | 13.9 | 0.15 | 1.1 | 9.0 |
| | 12.2 | 8.37 | 0.13 | 1.6 | 1.5 |
| Trifluoroacetato[d] | 102 | 69.7 | 0.090 | 0.13 | 0.16 |
| | 48.8 | 33.4 | 0.17 | 0.50 | 0.37 |
| | 24.4 | 16.7 | 0.10 | 0.60 | 0.70 |
| | 16.6 | 11.2 | 0.13 | 1.2 | 1.0 |
| | 12.2 | 11.53 | 0.17 | 1.5 | 1.3 |

[a] $k_{II} = k_{obsd}/[Ti(III)]$. [b] [Co(III)] = (2.0–3.5) × $10^{-4}$, λ = 502 nm. [c] [Co(III)] = (3.5–4.2) × $10^{-4}$ *M*, λ = 502 and 349 nm. [d] [Co(III)] = 4 × $10^{-4}$ *M*, λ = 349 nm. [e] $\mu$ = 1.7 *M*.

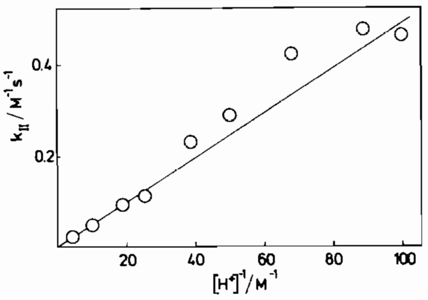

Fig. 1. Plot of the second order rate constant $k_{II}$ *vs.* $[H^+]^{-1}$ for the titanium(III) reduction of $Co(NH_3)_5(OOCCH_3)^{2+}$ at 25 °C and $\mu$ = 1.0 *M* ($H^+$, $Na^+$, $Cl^-$).

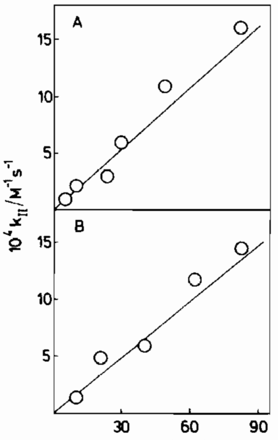

Fig. 2. Plot of the second order rate constant $k_{II}$ *vs.* $[H^+]^{-1}$ for the titanium(III) reduction of (A) $Co(NH_3)_5(OOCCCl_3)^{2+}$ and (B) $Co(NH_3)_5(OOCCF_3)^{2+}$ at 25 °C and $\mu$ = 1.0 *M* ($H^+$, $Na^+$, $Cl^-$).

## Results

The rate of the titanium(III) reduction of $Co(NH_3)_5(OOCR)^{2+}$, R = $CH_3$, $CF_3$, and $CCl_3$, was found to be first order in Co(III) and first order in Ti(III). The rate constants observed, $k_{obsd}$, at different acidities are presented in Table I. The run involving $Co(NH_3)_5(OOCCH_3)^{2+}$ at 1.0 *M* HCl and 1.7 *M* ionic strength (NaCl) gave the value of 4.1 × $10^{-3}$ $M^{-1}$ $s^{-1}$ for the second order rate constant, in satisfactory agreement with the value of 4.9 × $10^{-3}$ $M^{-1}$ $s^{-1}$ obtained by Martin and Gould at the same conditions but for *p*-toluenesulfonate medium [2].

The choice of the experimental acidity range was limited by several restrictions. The equilibrium constant for the protonation of acetate ligand coordinated in $Co(NH_3)_5(OOCCH_3)^{2+}$ at 25 °C and $\mu$ = 1.0 *M* is 0.25 $M^{-1}$ [8]. Due to an inductive effect of halogens the protonation constant for $Co(NH_3)_5(OOCCCl_3)^{2+}$ and $Co(NH_3)_5(OOCCF_3)^{2+}$ is probably lower. The experimental acidity of $\lesssim$0.2 *M* was used to keep the amount of protonated Co(III) species at $\lesssim$5%. The dissocation of the Co(II) redox product leads to a consumption of 5–6 mol-equivalents of protons, which limited experimental acidity to $\gtrsim$0.01 *M*. Within this acidity range the second order rate constant, $k_{II} = k_{obsd}/[Ti(III)]$, is proportional to the inverse acid concentration, as demonstrated in Figs. 1 and 2. The scatter of the data does not allow an estimate of whether there exists a subtle departure from the linearity in the figures, and the dependence is satisfactorily expressed by the general eqn. 1. A preliminary treatment of the data from Table I

$$k_{II} = k_o + k_{-1}[H^+]^{-1} \qquad (1)$$

according to eqn. 1 gave negative $k_o$ with a value within its standard deviation for all the three Co(III) species, indicating that the $k_o$ path is inoperative. The data were therefore treated according to eqn. 2, using

$$k_{II} = k_{-1}[H^+]^{-1} \qquad (2)$$

a non-linear least-squares computer program, giving $k_{-1}$ values (4.9 ± 0.3) × $10^{-3}$ $s^{-1}$, (1.8 ± 0.2) × $10^{-5}$ $s^{-1}$, and (1.6 ± 0.2) × $10^{-5}$ $s^{-1}$ for the titanium(III) reduction of $Co(NH_3)_5(OOCCH_3)^{2+}$, $Co(NH_3)_5(OOCCCl_3)^{2+}$, and $Co(NH_3)_5(OOCCF_3)^{2+}$, respectively. The uncertainties quoted are standard deviations. The average and maximal individual deviation of the experimental from the calculated $k_{II}$ value are 12.6% and 21% for $Co(NH_3)_5(OOCCH_3)^{2+}$, 15.8% and 29% for $Co(NH_3)_5(OOCCCl_3)^{2+}$, 18.4% and 32% for $Co(NH_3)_5(OOCCF_3)^{2+}$. The relative high average and maximal individual deviation of the $k_{II}$ values come from a lower than usual precision in evaluation of the experimental rate constants, due mostly to the slowness of the reaction (a number of runs was followed up to 20–25% completion).

## Discussion

The acidity dependence according to eqn. 2 of the second order rate constant for the titanium(III) reduction of $Co(NH_3)_5(OOCCH_3)^{2+}$, $Co(NH_3)_5(OOCCCl_3)^{2+}$, and $Co(NH_3)_5(OOCCF_3)^{2+}$ is in compliance with the observation made for a number of redox reactions that $TiOH^{2+}$ is the only or at least the predominant reacting species of titanium(III) in acidic aqueous media. The linearity of the plots in Figs. 1 and 2 for the acidity range studied is consistent with the value of (2–3.5) × $10^{-3}$ *M* for the acid dissociation constant of $Ti^{3+}$, $K_a$ [13–15]. The rate constants for the reduction by the $TiOH^{2+}$ species, $k_{TiOH}$, expressed then as $k_{-1}/K_a$ ($K_a$ = 3.5 × $10^{-3}$ *M* at 25 °C and $\mu$ = 1.0 *M*) [15] are listed in Table II and compared with the constants for some other reducing agents. The change in the reaction rate on going from $Co(NH_3)_5(OOCCH_3)^{2+}$ to $Co(NH_3)_5(OOCCF_3)^{2+}$ for the reduction by $TiOH^{2+}$ is strongly opposite in trend to the reduction by $Ru(NH_3)_6^{2+}$ and is similar in trend to the reduction by $Eu^{2+}$, $Cr^{2+}$, and $V^{2+}$, immediately indicating that reduction of the acetato complex by $TiOH^{2+}$ proceeds by an inner sphere mechanism. A run performed at $[H^+]$ = 1.0 *M* and $\mu$ = 1.7 *M* enabled Martin and Gould to reach a similar conclusion about the acetato complex using different arguments [2]. The expression, eqn. 3, correlating specific rates of outer sphere reductions of Co(III) complexes by $TiOH^{2+}$ and $Ru(NH_3)_6^{2+}$ has been derived [16].

$$\log (k_{TiOH}K_a) = \log k_{-1} = 0.40 \log k_{Ru} - 3.79 \qquad (3)$$

Using eqn. 3 outer sphere rates for the reduction of the three Co(III) complexes by $TiOH^{2+}$ have been calculated, as well as outer sphere fractions of the observed rates, and included in the last two columns of Table II. While the outer sphere fraction for the reduction of the acetato complex makes up for 0.7% of the observed rate, in agreement with the assignment of the inner sphere mechanism to this reaction, the calculated outer sphere rates for reduction of the trichloroacetato and trifluoroacetato complex are five times larger than the observed ones. We conclude that the two latter Co(III) complexes are reduced by $TiOH^{2+}$ in an outer sphere mode. The discrepancy with eqn. 3 may be reconciled by inspection of some additional data obtained for the outer sphere reduction of Co(III) complexes by $TiOH^{2+}$ and $Ru(NH_3)_6^{2+}$, which indicate that the coefficients in eqn. 3 may have to be reconsidered [17].

The ratio of the specific rates of the acetato and trifluoroacetato complex, listed in Table II, have relatively small values for the reductions by $Eu^{2+}$, $Cr^{2+}$, and $V^{2+}$, which have been shown to proceed by an inner sphere mechanism [18]. The ratio is >300, however, for the reduction by $TiOH^{2+}$, where the change from an inner sphere to the outer sphere mechanism occurs.

Titanium(III) was found to reduce a variety of carboxylatocobalt(III) complexes by an inner sphere mechanism [2–4], and a pertinent question is why in this case it behaves differently from $Eu^{2+}$, $Cr^{2+}$, and $V^{2+}$. The change from inner to outer sphere mechanism is most likely due to a larger span in stability constants of the binuclear precursor complexes formed by Ti(III) than the span in stability of the precursors formed by the other reductants. Steric hindrances to bridge formation with the halogenated acetato ligands are probably not sub-

TABLE II. The Second Order Rate Constants ($M^{-1}$ $s^{-1}$) for the Reduction of $Co(NH_3)L^{2+}$ at 25 °C and Some Rate Comparisons.

| L | pK[a] | Reducing Agent | | | | | Calculated OS[f] | Fraction OS[g] |
|---|---|---|---|---|---|---|---|---|
| | | $Ru(NH_3)_6^{2+}$ [b,c] | $Eu^{2+}$ [b,d] | $Cr^{2+}$ [b,d] | $V^{2+}$ [b,d] | $TiOH^{2+}$ [e] | $(TiOH^{2+})^{OS}_{calcd}$ | $(TiOH^{2+})^{OS}_{frac}$ |
| $CH_3COO^-$ | 4.53 | 0.022 | 1.7 | 0.35 | 1.25 | 1.4 | $1.0 \times 10^{-2}$ | 0.007 |
| $CCl_3COO^-$ | 0.7 | 0.25 | 0.82 | – | – | $5.1 \times 10^{-3}$ | $2.7 \times 10^{-2}$ | 5.22[h] |
| $CF_3COO^-$ | 0.3 | 0.18 | 1.3 | 0.034 | 0.86 | $4.5 \times 10^{-3}$ | $2.3 \times 10^{-2}$ | 5.07[h] |
| $\frac{k_{CH_3COO}}{k_{CF_3COO}}$ [i] | | 0.12 | 1.3 | 10 | 1.5 | 300 | 0.44 | – |

[a] K = acid dissociation constant of the uncoordinated ligand. [b] Data from ref. 18. [c] $\mu = 0.5$ *M*, LiCl. [d] $\mu = 1.0$ *M*, $LiClO_4$. [e] This work, $\mu = 1.0$ *M*, NaCl. [f] Rate constants for outer sphere reductions (OS) calculated from the relationship $\log (k_{TiOH}K_a) = \log k_{-1} = 0.4 \log_{Ru} - 3.79$ given in ref. 16. [g] Outer sphere fraction of the observed rate. [h] See text. [i] Ratio of the rate constants of the acetato and trifluoroacetato complex.

stantially different for $TiOH^{2+}$ from those for the congeners. The cause of a larger span in stability of Ti(III) precursors may lay in the substitution mechanism on the Ti(III) center. Substitutions are believed to proceed according to an associative mechanism [5–7], which makes formation rates of the Ti(III) precursors with a series of similar bridges sensitive to the nucleophilicity of a particular bridging ligand. The basicities of the free acetate and the halogenated acetate anions, Table II, are noticeably different. The difference, on another scale, is most likely also retained when these ligands are coordinated to pentaamminecobalt(III) ($K_{AH}$ of $Co(NH_3)_5(OOCCH_3)^{2+}$ is 0.25 $M^{-1}$ at 25 °C and $\mu = 1.0$ *M*) [8]. If it is assumed that basicities of the coordinated acetates parallel their nucleophilicities then the change in the reduction mechanism by $TiOH^{2+}$ can be rationalized.

## References

1 Taken from the *Ph.D. Thesis*, R. Marčec, University of Zagreb (1977).
2 A. H. Martin and E. S. Gould, *Inorg. Chem., 14,* 873 (1975).
3 A. H. Martín and E. S. Gould, *Inorg. Chem., 15,* 1934 (1976).
4 A. Hery and K. Wieghardt, *Inorg. Chem., 17,* 1130 (1978).
5 H. Diebler, *Proc. Int. Conf. Coord. Chem., 16,* S12 (1974).
6 H. Diebler, *Z. Phys. Chem., 68,* 64 (1969).
7 P. Chaudhuri and H. Diebler, *J. Chem. Soc. Dalton,* 596 (1977).
8 M. B. Barett, J. H. Swinehart, and H. Taube, *Inorg. Chem., 10,* 1983 (1971).
9 R. B. Jordan and H. Taube, *J. Am. Chem. Soc., 88,* 4406 (1966).
10 F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem., 24,* 1241 (1962).
11 A. Bakač and M. Orhanović, *Inorg. Chim. Acta, 21,* 173 (1976).
12 R. Marčec and M. Orhanović, *Inorg. Chem., 17,* 3672 (1978).
13 H. Kretzien and F. Brito, *Chem. Abstr., 73,* 7865 (1970).
14 M. R. Paris and C. L. Gregoire, *Anal. Chim. Acta, 42,* 439 (1968).
15 A. Bakač, R. Marčec, and M. Orhanović, *Inorg. Chem., 16,* 3133 (1977).
16 G. A. K. Thompson and A. G. Sykes, *Inorg. Chem., 15,* 638 (1976).
17 Reduction of $Co(terpy)_2^{3+}$ and $Co(phen)_3^{2+}$ by $TiOH^{2+}$ (ref. 15), by $Ru(NH_3)_6^{2+}$ (preliminary data obtained by V. Butković), and $k = 1.1 \times 10^4$ $M^{-1}$ $s^{-1}$ for $Ru(NH_3)_6^{2+}$ reduction of $Co(bipy)_3^{3+}$.
18 F. F. Fan and E. Gould, *Inorg. Chem., 13,* 2647 (1974).