From the DSC and TGA curves, it appears that the deamination at low catalyst levels is a two-step process. The first step of this process involves the loss of two molecules of en for each three molecules of complex. The intermediate is stable over about a 10 °C range of temperature. The second step involves the loss of one molecule of en for each three molecules of complex to give the final product. At the high catalyst levels, the deamination occurs in one step corresponding to loss of one molecule of en per molecule of complex, and in these higher temperature nonisothermal studies the thermal data are consistent with a cis product.

Registry No. $[Cr(en)_3](NCS)_3$, 14176-00-2; NH_4SCN, 1762-95-4.

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Kinetics and Mechanism of the Reduction of Iodo- and Bromopentaammineruthenium(III) by Titanium(III)

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The redox reactions of the halopentaammine complexes of cobalt(III) and ruthenium(III) with reductants such as chromium(II),[1] vanadium(II),[2-4] uranium(III),[5,6] europium(II),[2,3] tris(bipyridyl)chromium(II),[3] hexaammineruthenium(II),[7] aquapentaammineruthenium(II),[8] and titanium(III)[9,10] have been investigated extensively. The reactivity order has come to be known as "normal" or "inverse", depending on whether rate increases or decreases with increasing atomic number of the halogen. The normal reactivity order (I > Br > Cl) is observed for the reactions of chromium(II), vanadium(II), hexaammineruthenium(II), and tris(bipyridyl)chromium(II) with halopentaamminecobalt(III),[1,3] and for the reactions of uranium(III) and aquapentaammineruthenium(II) with halopentaammineruthenium(III).[6,8a] The inverse order (I < Br < Cl) is observed for the reactions of europium(II), iron(II), and uranium(III) with halopentaamminecobalt(III)[3-5] and for the reactions of chromium(II) and europium(II) with halopentaammineruthenium(III).[2] An unusual order (Cl > I > Br)[9,10] is observed for the reactions of titanium(III) with the halopentaamminecobalt(III) complexes, and Thompson and Sykes[10] have been able to assign an outer-sphere mechanism to the reactions by using modified Marcus theory plots.

Reactivity trends listed above are not diagnostic of mechanism since both inner-sphere and outer-sphere mechanisms apply to some of the reactions of normal and inverse orders. Haim[11] pointed out that the normal reactivity trend observed in the chromium(II)–halopentaamminecobalt(III) reactions is indicative of the relative stabilities of the halogen-containing transition states.

Chalilpoyil, Davies, and Earley[12] recently investigated the reactions of titanium(III) with chloropentaammineruthenium(III) and assigned[13] an outer-sphere mechanism to these, using linear free-energy plots. We here report studies of the reduction of iodo- and bromopentaammineruthenium(III) complexes by titanium(III). A reactivity trend is obtained and the ambiguous reactivity trend[8] criterion is avoided in assigning a mechanism to these reactions.

Experimental Section

Reagents were prepared and purified by standard procedures.[14,15] The spectra of the complexes $Ru(NH_3)_5Br^{2+}$ and $Ru(NH_3)_5I^{2+}$ agreed with those in the literature.[15] Pure titanium(III) chloride (Koch-Light Laboratories, Ltd.) was used as previously described.[16]

The reactions were monitored on an SP 500 spectrophotometer by following decreasing absorbances of the oxidants at the wavelength[6] of maximum absorption: $Ru(NH_3)_5Br^{2+}$, λ 398 nm, $\epsilon = 1.85 \times 10^3$ dm^3 mol^{-1} cm^{-1}; $Ru(NH_3)_5I^{2+}$ λ 545 nm, $\epsilon = 2.11 \times 10^3$ dm^3 mol^{-1} cm^{-1}. All runs were performed at 25.0 ± 0.1 °C under pseudo-first-order conditions in chloride and trifluoromethanesulfonate media, with $I = 1.0$ mol dm^{-3}. The reduction potentials of the chloro- and bromopentaammineruthenium(III) complexes are available in literature,[17,18] but that of the iodo complex is not available. It was therefore measured by using the method of Kallen and Earley,[19] in trifluoroacetate buffers.

Results

The observed rate constants are presented as functions of acid in Table I. The reactions are free of complications as judged from the linear pseudo-first-order plots. Rate constants obtained with chloride and trifluoromethanesulfonate as ionic strength media agree very well (Table I). Where the effects of anions (Cl^-, N^{3-}, SCN^-) were investigated, it was convenient therefore to use trifluoromethanesulfonate to maintain the ionic strength at 1.0 mol dm^{-3}.

In the acid concentration range 0.01–1.00 mol dm^{-3}, the observed second-order rate constant is inversely proportional to $[H^+]$. The data obtained therefore fit eq 1. This implies

$$k_{\text{obsd}} = a/[H^+] \qquad (1)$$

that $TiOH^{2+}$, rather than Ti^{3+}, is the predominant reducing species,[12] with $a = k_2K_a$, where K_a is the acidity constant of Ti^{3+} and k_2, the electron-transfer rate constant for $TiOH^{2+}$. Application of eq 1 to the data gave a as 0.28 ± 0.03 s^{-1} for the Ti(III)/$Ru(NH_3)_5Br^{2+}$ reaction and 0.56 ± 0.03 s^{-1} for the Ti(III)/$Ru(NH_3)_5I^{2+}$ reaction. Some measurements of k_{obsd} as a function of acid concentration at $[H^+] < 0.01$ mol dm^{-3} indicate that $K_a \approx 5 \times 10^{-3}$ mol dm^{-3}, in agreement with the value of K_a employed by Chalilpoyil, Davies, and Earley[12] to calculate k_2. When this value for the acidity constant K_a is employed for Ti^{3+}, k_2 for the Ti(III)/$Ru(NH_3)_5Br^{2+}$ and Ti(III)/$Ru(NH_3)_5I^{2+}$ reactions are 56.0 ± 5.3 dm^3 mol^{-1} s^{-1} and 112.0 ± 6.2 dm^3 mol^{-1} s^{-1}, respectively.

The effects of added anions (Cl^-, N_3^-, SCN^-) on the reactions of Ti(III) with bromopentaammineruthenium(III) were investigated. The anions catalyze the reaction in the order $SCN^- \gg N_3^- > Cl^-$ (Table II). The reduction potential ($\mathcal{E}°$, mV vs. NHE) of the iodopentaammineruthenium(III) complex (which was measured as the average of the cathodic and anodic peak potentials in ~1 mol dm^{-3} $CF_3COOH/LiCF_3COO$ solutions, pH 2–3, sweep rate ~20 V/s) is −21.

Discussion

These results further testify to the characteristic hydrolytic[12,16] behavior of Ti(III), in which $TiOH^{2+}$ is the predominant reactive component. Since the value of k_2 obtained by Chalilpoyil, Davies, and Earley for the Ti(III)/$Ru(NH_3)_5Cl^{2+}$ reaction[12] is 12.0 dm^3 mol^{-1} s^{-1} and those obtained for the Ti(III)/$Ru(NH_3)_5Br^{2+}$ and Ti(III)/Ru-

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Table I. Acid Dependence of the Rate Constants for the Reduction of Iodo- and Bromopentaammineruthenium(III) by Ti(III)[a]

$10^4[Ti^{III}]$, mol dm^{-3}	$[H^+]$, mol dm^{-3}	$10^4 k_1$, s^{-1}	k_{obsd}, dm^3 mol^{-1} s^{-1}
A. $[Ru(NH_3)_5Br^{2+}] = 2.03 \times 10^{-5}$ mol dm^{-3}			
1.97	0.010	56.1	28.5
2.53	0.010	71.3	28.2
2.67	0.010	74.2	27.8
2.71	0.010	78.0	28.8
2.74	0.012	62.5	22.8
2.53	0.015	44.3	17.5
2.70	0.020	41.6	15.4
2.46	0.025	27.6	11.2
2.46	0.032	23.6	9.6
2.46	0.050	13.8	5.6
2.53	0.075	12.7	5.0
2.11[b]	0.100	5.5	2.6
2.11	0.100	5.9	2.8
3.06[b]	0.100	9.2	3.0
3.06	0.100	8.0	2.6
5.06	0.100	13.7	2.7
10.20	0.150	17.3	1.7
10.20	0.200	14.3	1.4
10.20	0.250	10.2	1.0
12.30	0.300	8.6	0.7
17.40	0.500	7.0	0.4
20.40	0.600	6.1	0.3
26.70	1.000	5.3	0.2
B. $[Ru(NH_3)_5I^{2+}] = 2.13 \times 10^{-5}$ mol dm^{-3}			
2.18	0.010	121.6	55.8
2.18	0.012	100.5	46.1
2.18	0.015	85.5	39.2
3.54	0.020	93.8	26.5
2.62	0.025	57.4	21.9
3.54	0.040	51.3	14.5
3.54	0.060	37.5	10.6
3.54	0.080	23.0	6.5
4.50	0.100	25.2	5.6
4.50[b]	0.100	23.9	5.3
9.00	0.200	26.1	2.9
9.17	0.400	16.5	1.8
9.17	0.500	11.9	1.3
13.75	0.800	12.4	0.9
13.75	1.000	8.3	0.6

[a] $t = 25$ °C, $I = 1.0$ mol dm^{-3} (LiCl). [b] $I = 1.0$ mol dm^{-3} ($LiCF_3SO_3$).

Table II. Anion Dependence of the Rate Constants for the Reduction of Bromopentaammineruthenium(III) by Ti(III)[a]

A. $[Ti^{III}] = 4.36 \times 10^{-5}$ mol dm^{-3}

$[Cl^-]$, mol dm^{-3}	k_1, s^{-1}	k_{obsd}, dm^3 mol^{-1} s^{-1}
0.02	0.83	0.19
0.04	1.1	0.26
0.10	1.2	0.28
0.40	5.2	1.20
0.60	6.3	1.44
0.80	7.8	1.79
1.00	13.0	2.99

B. $[Ti^{III}] = 1.81 \times 10^{-4}$ mol dm^{-3}

$[N_3^-]$, mol dm^{-3}	k_1, s^{-1}	k_{obsd}, dm^3 mol^{-1} s^{-1}
0.01	0.54	0.30
0.02	0.63	0.35
0.04	1.1	0.60
0.08	7.8	4.31
0.10	13.0	7.20

C. $[Ti^{III}] = 1.36 \times 10^{-4}$ mol dm^{-3}

$[SCN^-]$, mol dm^{-3}	k_1, s^{-1}	k_{obsd}, dm^3 mol^{-1} s^{-1}
0.01	32.1	23.6
0.02	44.2	32.5
0.04	70.2	51.6

[a] $t = 25$ °C, $I = 1.0$ mol dm^{-3} ($LiCF_3SO_3$); $[Ru(NH_3)_5Br^{2+}] = 1.81 \times 10^{-5}$ mol dm^{-3}, $[H^+] = 0.1$ mol dm^{-3}.

$(NH_3)_5I^{2+}$ reactions are 56.0 ± 5.3 dm^3 mol^{-1} s^{-1} and 112.0 ± 6.2 dm^3 mol^{-1} s^{-1}, respectively, under the same conditions, the reactivity order is I > Br > Cl, which is a "normal" reactivity order for the halopentaammine complexes. This order does not, however, suggest outer-sphere or inner-sphere mechanisms for these reactions, as has been pointed out earlier by some workers[5,6,11] and may merely suggest the relative stabilities of the halogen-containing transition states.

The reduction potentials (mV vs. NHE) of the halopentaammineruthenium(III) complexes are as follows: $Ru(NH_3)_5Cl^{2+/+}$ (−59[17]), $Ru(NH_3)_5Br^{2+/+}$ (−34[18]), $Ru(NH_3)_5I^{2+/+}$ (−21, this work). The electron-transfer rate constants (k_2) obtained for the titanium(III) reduction of these complexes therefore increase in the direction of increasing reduction potentials—Cl < Br < I. The values of k_2 calculated using the suggested[13] more appropriate form of the linear free-energy relation in the form of eq 2 (where $°k$ is the rate

$$\log k - \log {}^{\circ}k = 0.48\frac{\mathcal{E}^{\circ}}{59} + \beta\left(\frac{\mathcal{E}^{\circ}}{59}\right)^2 \qquad (2)$$

constant at the zero of potential, $\mathcal{E}°$ is the reduction potential of the oxidant, and β is a constant) are 53.8 and 70.0 dm^3 mol^{-1} s^{-1} for the bromo- and iodopentaammineruthenium(III) complexes, respectively, with the condition that $\log {}^{\circ}k \approx 2.0$ and $\beta = 0.01$. When these are compared with the measured values, there is good agreement for the bromo complex (56.0 ± 5.3 dm^3 mol^{-1} s^{-1}), but less so for the iodo complex (112.0 ± 6.2 dm^3 mol^{-1} s^{-1}). However, the agreement is sufficient to infer a linear free-energy correlation for the bromo- and iodopentaammineruthenium(III) complexes as has been established for the outer-sphere reduction[13] of the chloropentaammineruthenium(III) and the other ruthenium(III) complexes by titanium(III). This is in contrast to the oxalato and acetato complexes of ruthenium(III) for which the very high reactivities[17] above the low reduction potential levels have been ascribed to "bridging".

An outer-sphere process is often implied when both oxidant and reductant are inert to substitution over the electron-transfer period.[8,20] Pecsok and Fletcher have suggested the absence of inner-sphere complexing of titanium(III) with bromide and iodide ions[21] since the absorption spectra of titanium(III) remains unchanged in these media as well as in noncomplexing perchlorate medium, over a large concentration range. It could be said therefore that titanium(III) is inert toward bromide and iodide substitution. This could be more so when bromide and iodide are coordinated to ruthenium(III) as in these halopentaammineruthenium(III) complexes. The halopentaammineruthenium(III) complexes aquate[22,23] at rates that are very slow compared with the obtained pseudo-first-order rate constants (k_1) for the corresponding electron-transfer reactions (ref 12 and Table I) in this work. An outer-sphere mechanism is therefore applicable to the titanium(III) reduction of these halopentaammineruthenium(III) complexes.

The pronounced accelerating effects of added anions (Table II) for these reactions is indicative of an outer-sphere mechanism as has been observed for some outer-sphere reactions.[6,16,24,25] This is in contrast to the smaller effects observed in an inner-sphere mechanism.[6,24,25] Outer-sphere-activated complexes are stabilized by the various added anions to markedly different extents with thiocyanate being the most exceptional. The different marked stabilizing effects exerted by these anions on the outer-sphere transition states are indicated by previous equilibrium studies involving titanium(III), thiocyanate, and chloride ions, which give the stability constants for the complexing of thiocyanate and chloride ions with titanium(III) as 1.5 ± 0.1[26] $dm^3\ mol^{-1}$ and 0.07–0.2[27] $dm^3\ mol^{-1}$ at 25 °C, respectively.

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Registry No. $Ru(NH_3)_5Br^{2+}$, 21388-15-8; $Ru(NH_3)_5I^{2+}$, 25483-95-8; Ti(III), 22541-75-9; Cl^-, 16887-00-6; N_3^-, 14343-69-2; SCN^-, 302-04-5.

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Reaction of Iron Pentacarbonyl with Oxygen-18-Enriched Hydroxide. Decarboxylation vs. Oxygen Exchange in the [Fe(COOH)] Intermediate

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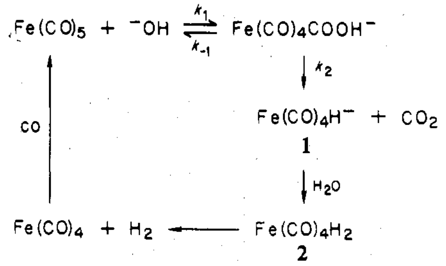
Recently iron pentacarbonyl in basic media has been demonstrated to effectively catalyze the water–gas shift and hydroformylation reactions.[1–3] These processes proceed by nucleophilic attack of hydroxide ion at a carbon center in $Fe(CO)_5$ resulting in formation of the intermediate $[Fe(CO)_4(COOH)^-]$ (see Scheme I). Subsequently this species undergoes decarboxylation to afford $Fe(CO)_4H^-$ (**1**) and carbon dioxide. Protonation of **1** leads to $Fe(CO)_4H_2$ (**2**) which can sustain reductive elimination of H_2 with addition of CO to re-form $Fe(CO)_5$ or react with olefins to give products of hydroformylation.[1,4,5] Evidence for hydroxide ion attack at a metal-bound carbon monoxide ligand has been obtained from oxygen-exchange studies.[6–11]

Scheme I



We report here reactivity studies of $Fe(CO)_5$ with oxygen-18-enriched hydroxide ion in an attempt to characterize this rather interesting and important process more completely.

Experimental Section

Materials. Iron pentacarbonyl was obtained from Strem Chemicals and was purified by vacuum distillation prior to use. $H_2{}^{18}O$ (99.0% by weight oxygen-18) was obtained from Norsk Hydro (Norway).

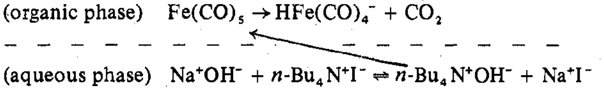
Preparation of [PPN][HFe(CO)$_4$]. The synthesis of $[PPN][HFe(CO)_4]$ was carried out in dry Schlenkware under a nitrogen atmosphere.[12] In a given run, 1.0 mmol of $Fe(CO)_5$ was dissolved in methanol and 4.0 mmol of $Na^{16}OH$ in 0.4 mL of $H_2{}^{18}O$ was added (upon equilibration the NaOH is 83.9% by weight oxygen-18). Stirring of the solution for 0.5 h and the addition of 1.0 mmol of PPNCl yielded a precipitate which redissolved in hot ethanol/ethyl acetate. Light yellow crystals were obtained upon cooling. An identical preparation of $[PPN][HFe(CO)_4]$ was performed by employing $H_2{}^{16}O$ for comparative purposes.

In order to decrease the base concentration during the synthesis of $[PPN][HFe(CO)_4]$, the reaction was carried out under phase-transfer conditions.[10] One millimole of $Fe(CO)_5$ and 0.028 mmol of $n\text{-}Bu_4NI$ in 5.0 mL of benzene were stirred vigorously with 5.0 mmol of NaOH in 0.40 mL of $H_2{}^{18}O$ (NaOH 80.8% by weight oxygen-18) for 14 h at room temperature. Volatiles were removed under vacuum (including much unreacted $Fe(CO)_5$) followed by workup as a methanol solution (vide supra) resulting in isolation of a small quantity of $[PPN][HFe(CO)_4]$.

Infrared Spectra. The infrared spectra were recorded on a Perkin-Elmer 521 spectrophotometer equipped with a linear-absorbance potentiometer. The spectra were calibrated against a water-vapor spectrum below 2000 cm^{-1} and against a CO spectrum above 2000 cm^{-1}. Sodium chloride solution cells (0.1 mm) were used with the appropriate solvent in the reference cell.

Results and Discussion

The infrared spectra in the ν(CO) region of $[PPN][HFe(CO)_4]$ prepared from both oxygen-18-labeled and unlabeled aqueous NaOH are illustrated in Figure 1. Analysis of these spectra indicates that there was no significant enhancement of ν(CO) vibrations attributable to $C^{18}O$-bound ligands when the reaction was run in highly enriched $Na^{18}OH/H_2{}^{18}O$. Therefore, the rate of the intermediate, $[Fe(CO)_4COOH^-]$, proceeding to $Fe(CO)_4H^-$ and CO_2 is rapid relative to reversible loss of ^-OH with concomitant oxygen exchange. Since it has previously been noted that the process leading to metal–hydride formation, when compared with that of oxygen-exchange, can be accelerated as a function of the added base concentration,[11] it was of interest to carry out the reaction under phase-transfer conditions where the hydroxide ion concentration is small (eq 1).[10] The large, lipophilic quaternary ion is soft in the HSAB sense,[13] thus preferring to ion-pair with the softer iodide ion instead of the hydroxide ion (i.e., the aqueous-phase reaction as written in eq 1 lies far to the left). Nevertheless, a small quantity of OH^- is transferred into the organic phase resulting in a low-yield production of


(1)

$$\text{(organic phase)}\quad Fe(CO)_5 \rightarrow HFe(CO)_4{}^- + CO_2$$
$$\text{(aqueous phase)}\quad Na^+OH^- + n\text{-}Bu_4N^+I^- \rightleftharpoons n\text{-}Bu_4N^+OH^- + Na^+I^-$$

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