

Kinetics and the mechanism of iron(II) reduction of *cis*- α -halogeno(cetylamine)(triethylenetetramine)cobalt(III) complex ion in aqueous acid medium

Kannappan Santhakumar*

Ecole Polytechnique Fédérale de Lausanne, EPFL-ENAC- LPAS, Station 6, CH-1015 Lausanne, Switzerland

Narayanasamy Kumaraguru and Sankarlingam Arunachalam

School of Chemistry, Bharathidasan University, Tiruchirappalli, 620 024 Tamil Nadu, India

Mahadevimanglam Narayanasamy Arumugham

Department of Chemistry, Vellore Institute of Technology, Vellore, 632 014 Tamil Nadu, India

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Abstract

The kinetics and mechanism of iron(II) reduction of *cis*- α -chloro/bromo(cetylamine)(triethylenetetramine)cobalt(III) surfactant complex ions were studied spectrophotometrically in an aqueous acid medium by following the disappearance of Co^{III} using an excess of the reductant under pseudo-first-order conditions: $[\text{Fe}^{\text{II}}] = 0.25 \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$, $[\mu] = 1.0 \text{ mol dm}^{-3}$ ionic strength in a nitrogen atmosphere at 303, 308 and 313 K. The reaction was found to be second order and showed acid independence in the range $[\text{H}^+] = 0.05\text{--}0.25 \text{ mol dm}^{-3}$. The second order rate constant increased with Co^{III} concentration and the presence of aggregation of the complex itself altered the reaction rate. The effects of $[\text{Fe}^{\text{II}}]$, $[\text{H}^+]$ and $[\mu]$ on the rate were determined. Activation and thermodynamic parameters were computed. It is suggested that the reaction of $\text{Fe}^{2+}(\text{aq})$ with Co^{III} complex proceeds by an inner-sphere mechanism.

Introduction

Electron transfer (ET) processes are fundamentally important to many branches of chemistry and biology. A feature of modern coordination chemistry is its expanding ability to mimic form and structure in biology. This had largely been achieved using a principle which had itself been borrowed from biology: the self-assembly of well-defined and complex molecular entities from constituent subunits in solution. Unlike biology, however, self-assembly in coordination chemistry occurs through the formation of coordinate bonds rather than weak inter- or intramolecular interactions. Self-assembly in coordination chemistry consequently provides an important and powerful entry into supramolecular engineering and the associated fields of solid-state and crystal engineering [1, 2]. It potentially also affords novel catalytic systems [3] which may ultimately be induced to offer the selectivity and usefulness of biological catalysts. Recently, there has been a growing interest in the study of processes under conditions globally referred to as restricted geometry, that is under conditions in which a given ligand was forced (or different ligands were forced) to remain, totally or partially, bound at the surface of some substrate. In a

broad sense, the restricted geometry conditions encompass phenomena such as heterogeneous catalysis [4], enzymatic catalysis [4], reactivity in micellar systems and microemulsions [5], molecular machines [6], molecular electronics [7], trapping of substrates by polyelectrolytes [8], conformational changes of DNA induced by the binding of solutes [9] and so forth. Numerous studies have been performed addressing the dependence of ET on different environments including metalloproteins [10], Vitamin B₁₂ [11], liquids [12, 13], micelles [14], vesicles [15] and DNA [16]. It was well known that amphiphilic molecules were characterized by their dual nature. In the same molecule two differentiated parts, the hydrocarbon (hydrophobic) and the ionic (hydrophilic), were found. This general structure, characteristic of surfactants, was responsible for the self-assembly process in solution. In the last century numerous works were performed on the nature of the self-assembly process and the interactions of these structures with salts, alcohols, proteins and other compounds [5]. A growing number of applications have been developed to study the metallosurfactants in this context. Surface-active materials were major building blocks of many physical, chemical and biological systems. They were introduced into several commercial products such as antiseptic agents in cosmetics and as germicides [17], and also found a wide range of

* Author for correspondence: E-mail: lovingsantha@yahoo.com

applications because of their unique solution properties such as detergency, solubilization and surface wetting capabilities, in diverse areas such as mining, petroleum and pharmaceutical industries. It has been observed [18–22] that several redox reactions in micellar media were influenced by the hydrophobic and electrostatic forces and for a given set of reactions the observed rate depends on the extent of association between the reactants and micellar aggregates. Most of the chemical reactions investigated were simple organic and inorganic systems. On the other-hand, relatively few works have been carried out on the electron-transfer reactions for transition metal ions complexes with lipophilic ligands [23–28]. Redox reactions of metallo-surfactants have been the subject of continued interest in their own right, especially in the context of ET processes. Owing to their importance in molecular synthesis and electrochemical reactions in a wide range of homogeneous and heterogeneous processes in many chemical and biochemical systems, ET reactions have been the subject of many theoretical and experimental studies. Most reactions of inorganic complexes in micellar and in microemulsion systems occur at rates markedly different from those in aqueous solution. During the course of studying the effects of metallo-surfactants on chemical reactions, catalytic effects were observed [29–32] above their critical micelle concentration (CMC). Such systems offered the possibility to investigate the effects of the local reactant concentrations in the micellar subphase, as well as the local microenvironment on the reactivity. Cobalt(III) complexes, by virtue of their abundance and diversity, have played a fundamental role in our understanding of the structural, spectroscopic and electrochemical properties of coordination compounds. We were interested in the synthesis and micelle forming properties of Co^{III} complexes containing lipophilic ligands for a long time [31–34]. As in biology, such compounds may exhibit novel physical and chemical properties with interesting and useful associated applications. Studies on the ET chemistry of Co^{III} metallosurfactants have received a sustained high level of attention, due to their relevance in various redox processes in biological systems and act as promising agents for antitumor [35], anthelmintic [36], antiparasitic [37], antibiotic [38] and antimicrobial activities [16]. In this study some of the interesting results concern the kinetics of electron transfer between Co^{III} metallosurfactants with Fe^{II} in aqueous acid medium.

Experimental

Materials

NaClO₄ was obtained from Fluka; other reagents were from Merck were used as received. The deionized H₂O used had conductivity <10⁻⁶ S m⁻¹ and was obtained from a Milli-Q water system. Pure N₂ gas was bubbled

through the reaction solutions to remove dissolved O₂. Oxidant solutions were shielded from light with aluminium foil.

Preparation of oxidant

The Co^{III} complexes, *cis-α*-[Co(trien)(C₁₆H₃₃NH₂)Cl](ClO₄)₂ and *cis-α*-[Co(trien)(C₁₆H₃₃NH₂)Br](ClO₄)₂, were used as oxidants and were synthesized by a similar method to that report earlier [33]. Their purity was assessed by UV–Visible spectroscopy and CHN analysis (Table 1).

Safety note: Caution! Perchlorate salts of Co^{III} complexes containing organic ligands are potentially explosive! Although we have experienced no problems with the compounds reported in this work, they should only be handled in small quantities and never scraped from sintered glass frits nor heated in the solid state.

Preparation of reductant

A stock solution of Fe(ClO₄)₂ was prepared by dissolving pure Fe powder in a slight excess of HClO₄ under a N₂ atmosphere. These solutions were prepared just prior to use for kinetic measurements. The ionic strength of the solution was adjusted by the addition of NaClO₄. The concentrations of Fe²⁺, H₂ and perchlorate ions in solution were determined by a method similar to that reported in the literature [39].

The free-acid content of iron solution was measured by passing it through a Dowex 50 W X-8 strong cation-exchange resin in the H⁺ form to obtain [H⁺] equivalent to the metal-ion concentration along with free acid, and then subtracting the metal equivalent from these. An aqueous solution of NaClO₄ was standardized by passage through a Dowex 50 W X-8 strong cation-exchange resin in the H⁺ form and titrating the liberated acid with standard NaOH to a phenolphthalein end-point. The total acid content of the reaction mixtures was calculated as added acid plus that produced by the hydrolysis of ferric ion.

Kinetic measurements

The reactant solution (containing the complex, NaClO₄, and HClO₄) was made up, omitting iron(II), and was thermostatted. A 1 cm path length cuvette was used to achieve optimum optical densities at the concentrations chosen. All the solutions were degassed in order to avoid any Fe^{II} air oxidation. After thorough purging with pure N₂ for *ca.* 30 min, the Fe^{II} solution was transferred to the cuvette sealed with a serum cap. A pool of Hg was created on the membrane of the cap to minimize leakage of air while introducing the requisite amount of Fe^{II} with a hypodermic syringe to initiate reaction and was followed on a Varian Cary 500 Scan UV-Vis-NIR spectrophotometer equipped with the Water Peltier System (PCB 150). The temperature was controlled within ±0.01 K. The decrease in the

absorbance was followed at the maximum visible absorption of the Co^{III} complex. All kinetic measurements were performed under pseudo-first-order conditions with the Fe^{II} in excess over the Co^{III} complex. The concentration of $\text{Fe}(\text{ClO}_4)_2$ used was 0.25 mol dm^{-3} and the concentration of Co^{III} complex was chosen typically above their CMC values in the $3.0\text{--}7.0 \times 10^{-3} \text{ mol dm}^{-3}$ region. The ionic strength was maintained at 1.0 M in all the runs using NaClO_4 . Studies were also carried out in the absence of Fe^{II} where the absorbance of the complex was monitored as a function of time for the same period. As in the case of the redox studies, no change in the absorbance was noted. The second-order rate constant, k , for the Fe^{II} reduction of the Co^{III} complex defined by $-\text{d}[\text{Co}^{\text{III}}]/\text{d}t = k[\text{Co}^{\text{III}}][\text{Fe}^{\text{II}}]$ was calculated from the concentration of iron(II) and the slope of the $\log(A_t - A_x)$ versus time plot, which is equal to $-k[\text{Fe}^{2+}]/2.303$, where A_t is the absorbance at time t ; A_x , the absorbance after all the Co^{III} complex has been reduced to Co^{II} , and k , the rate constant. Usually the value of A_x was measured at times corresponding to 10 half-lives. All the first-order plots were linear, with a correlation coefficient of 0.999. Each rate constant reported was the average result of triplicate runs. Rate constants obtained from successive half-life values within a single run agreed to within $\pm 5\%$. No trends indicative of systematic errors were noted, and the average values did not differ significantly from those obtained from least-squares treatment of logarithmic plots of absorbance differences against reaction time.

Effect of $[\text{Fe}^{2+}]$

Figure 1 gives the pseudo-first-order rate constant (k_p) for a series of runs at various concentrations of Fe^{II}

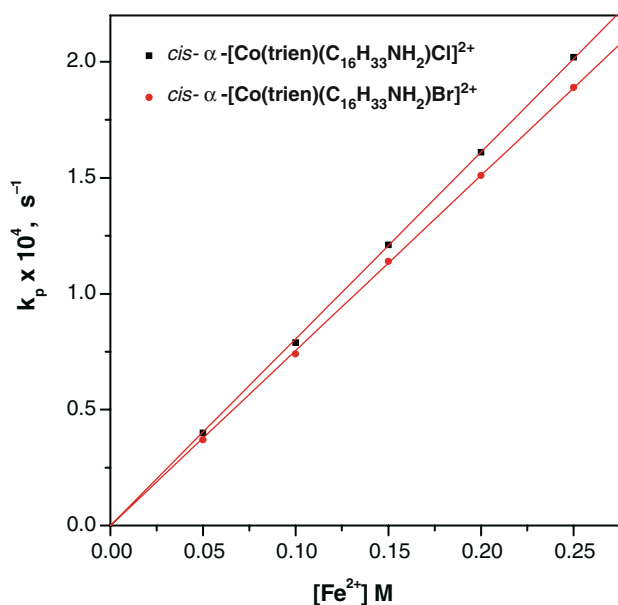


Fig. 1. Effect of $[\text{Fe}^{2+}]$ on pseudo-first-order rate constants: ($[\text{Co}^{\text{III}}] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\mu] = 1.0 \text{ mol dm}^{-3}$; $[\text{H}^+] = 0.10 \text{ mol dm}^{-3}$, Temp = 308 K).

for the chloro/bromo systems at fixed Co^{III} concentration. Plots of $\log(A_t - A_x)$ versus time were linear and the pseudo-first-order rate constant ($k_p, \text{ s}^{-1}$) evaluated from these plots was found to increase with an increase in $[\text{Fe}^{2+}]$. This shows that the reaction is first order with respect to $[\text{Fe}^{2+}]$. Plots of $k_p (\text{ s}^{-1})$ versus $[\text{Fe}^{2+}]$ generated straight lines, passing through origin, confirming the first-order dependence of reaction rate with respect to $[\text{Fe}^{2+}]$. Such a kinetic behaviour, with no intercept in the plots of $k_p (\text{ s}^{-1})$ versus $[\text{Fe}^{2+}]$, indicates that the complex formed is too unstable to be detected. Independence of the calculated values of k upon the concentration of Fe^{II} confirms the second order kinetics.

Stoichiometry

The stoichiometry of the reaction was determined by estimating the Fe^{III} and Co^{II} present in the product mixture. Fe^{III} was determined spectrophotometrically by Kitson's method [40] and Co^{II} was determined [41] as $[\text{CoCl}_4]^{2-}$ at 690 nm in an excess of HCl. The ratio $\text{Fe}^{\text{III}} : \text{Co}^{\text{II}}$ was found to be 1:1 in the reactions studied, indicating 1:1 stoichiometry.

Results and discussion

CMC values

The detailed procedure and the various thermodynamic properties for many Co^{III} metallosurfactants were previously discussed in our earlier reports [31–34]. The CMC values along with various thermodynamic properties for the complexes under investigation which were presented in Table 2 and Figure 2 were obtained by conductivity studies in aqueous solution.

Electron-transfer kinetics

Kinetic data obey the rate equation first order with respect to both the Co^{III} complex and Fe^{II} ,

$$-\text{d}[\text{Co}^{\text{III}}]/\text{d}t = -\text{d}[\text{Fe}^{\text{II}}]/\text{d}t = k[\text{Co}^{\text{III}}][\text{Fe}^{\text{II}}]$$

corresponding to the chemical process (Scheme 1), since FeX^{2+} is the only Fe^{III} species produced in the reaction, although it would dissociate into Fe^{3+} and X^- under experimental the conditions.

Table 3, shows the values of the measured second-order rate constant of the specific rates of $\text{cis-}\alpha\text{-Co}(\text{trien})(\text{C}_{16}\text{H}_{33}\text{NH}_2)\text{X}^{2+}$ with Fe^{2+} at three different temperatures (303, 308 and 313 K) in aqueous solution at fixed $[\text{Fe}^{2+}]$, ionic strength and acid concentration. In all cases, $\log(A_t - A_x)$ versus t plot were substantially linear for at least 2 half-lives. The second-order rate constant for the Fe^{2+} reduction of Co^{III}

Table 3. Second order rate constants for the reduction of $[\text{Co}^{3+}]$ by $[\text{Fe}^{2+}]$ in aqueous solution

Oxidizing agent	$[\text{Co(III)}] \times 10^3 \text{ mol dm}^{-3}$	$k \times 10^4 (\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$		
		303 K	308 K	313 K
<i>cis</i> - α - $[\text{Co}(\text{trien})(\text{C}_{16}\text{H}_{33}\text{NH}_2)\text{Cl}]^{2+}$	3.0	0.62 ± 0.2	3.91 ± 0.1	5.49 ± 0.1
	4.0	0.80 ± 0.1	5.22 ± 0.2	9.05 ± 0.3
	5.0	0.91 ± 0.3	6.70 ± 0.3	10.12 ± 0.4
	6.0	1.12 ± 0.1	8.10 ± 0.2	12.25 ± 0.2
	7.0	3.10 ± 0.2	9.42 ± 0.1	15.43 ± 0.1
<i>cis</i> - α - $[\text{Co}(\text{trien})(\text{C}_{16}\text{H}_{33}\text{NH}_2)\text{Br}]^{2+}$	3.0	0.51 ± 0.3	3.03 ± 0.4	5.20 ± 0.1
	4.0	0.60 ± 0.1	4.88 ± 0.2	8.04 ± 0.3
	5.0	0.82 ± 0.2	6.14 ± 0.1	9.51 ± 0.1
	6.0	1.06 ± 0.2	7.58 ± 0.2	11.31 ± 0.2
	7.0	2.12 ± 0.1	8.34 ± 0.1	14.14 ± 0.2

$[\text{Fe(II)}] = 0.25 \text{ mol dm}^{-3}$; $[\mu] = 1.0 \text{ mol dm}^{-3}$ (NaClO_4); $[\text{H}^+] = 0.10 \text{ mol dm}^{-3}$.

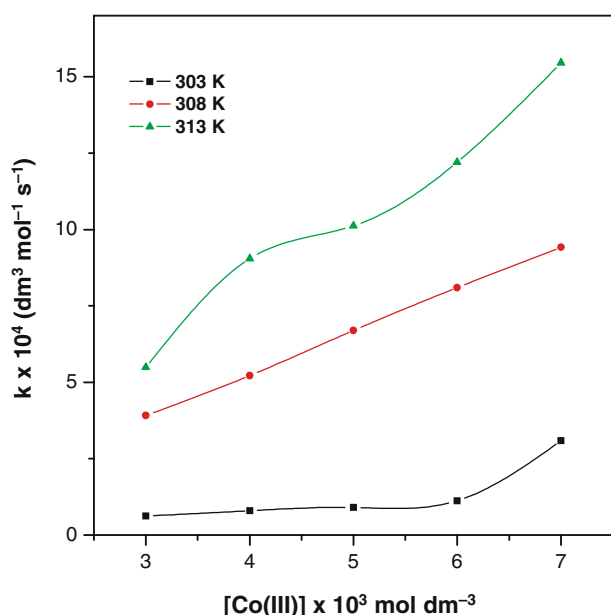


Fig. 3. Plot of $[\text{Co}(\text{trien})(\text{C}_{16}\text{H}_{33}\text{NH}_2)\text{Cl}]^{2+}$ versus k , ($[\text{Fe}^{\text{II}}] = 0.25 \text{ mol dm}^{-3}$; $\mu = 1.0 \text{ mol dm}^{-3}$ (NaClO_4); $[\text{H}^+] = 0.10 \text{ mol dm}^{-3}$).

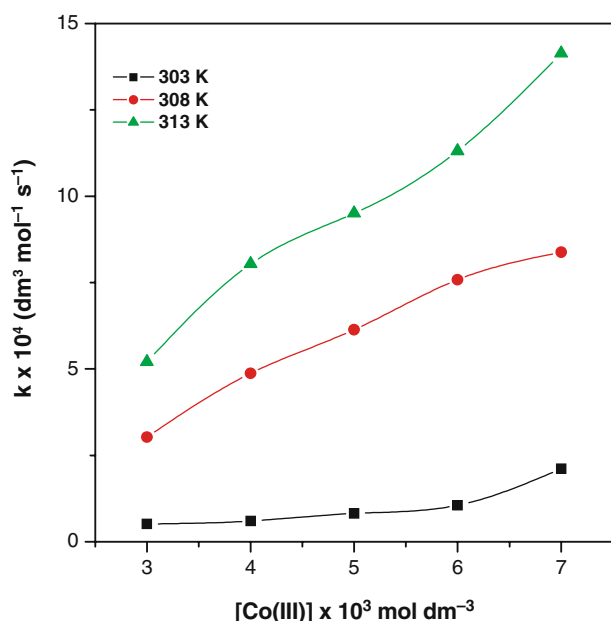


Fig. 4. Plot of $[\text{Co}(\text{trien})(\text{C}_{16}\text{H}_{33}\text{NH}_2)\text{Br}]^{2+}$ versus k , ($[\text{Fe}^{\text{II}}] = 0.25 \text{ mol dm}^{-3}$; $\mu = 1.0 \text{ mol dm}^{-3}$ (NaClO_4); $[\text{H}^+] = 0.10 \text{ mol dm}^{-3}$).

constant at 6.0×10^{-3} , 0.25 mol dm^{-3} and 308 K , respectively. In each case the ionic strength was maintained constant at 1.0 mol dm^{-3} by the addition of NaClO_4 . The results obtained indicate that the second-order rate constant was independent of the hydrogen-ion concentration (Figure 5). Such a kinetic behaviour indicates the nonexistence of any protonation equilibrium with respect to both $[\text{Fe}^{2+}]$ and $[\text{Co}^{3+}]$ under the prevailing experimental conditions.

Effect of ionic strength (μ)

The influence of varying the concentration of ionic strength on the reaction rate was studied by the addition of NaClO_4 from 0.50 to 2.0 mol dm^{-3} keeping $[\text{Co}^{\text{III}}]$, $[\text{Fe}^{\text{II}}]$, $[\text{H}^+]$ and temperature constant at 6.0×10^{-3} , 0.25 , 0.10 mol dm^{-3} and 308 K , respectively. The value of k was found to increase with an increase in ionic strength. (Figure 6).

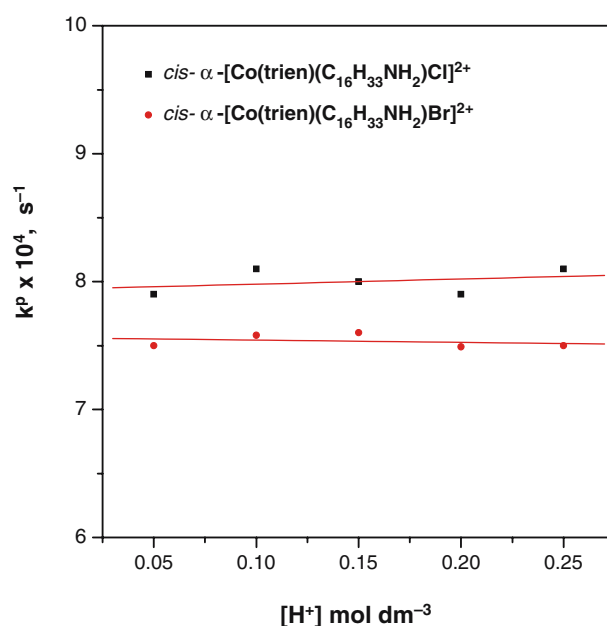


Fig. 5. Effect of $[\text{H}^+]$ on k , ($[\text{Co}^{\text{III}}] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{Fe}^{\text{II}}] = 0.25 \text{ mol dm}^{-3}$; $[\mu] = 1.0 \text{ mol dm}^{-3}$; $[\text{H}^+] = \text{HClO}_4 \text{ mol dm}^{-3}$; Temp = 308 K).

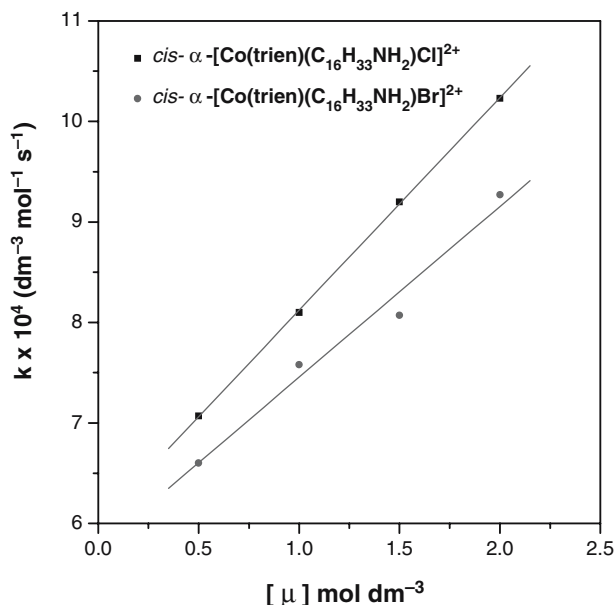


Fig. 6. Effect of Ionic strength on k , ($[\text{Co}^{\text{III}}] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{Fe}^{\text{II}}] = 0.25 \text{ mol dm}^{-3}$; $\mu = (\text{NaClO}_4)$; $[\text{H}^+] = 0.10 \text{ mol dm}^{-3}$; Temp = 308 K).

Nonbridging ligand effect

Nonbridging ligand effects were previously classified [42, 43] in the following three categories; (a) effects of geometry – relative rates of reduction of various pairs of *cis* and *trans* isomers; (b) effects of changing the nature of one nonbridging ligand – variation in rates along a series of constant *cis* or *trans* geometries; (c) effects of chelation – change in rate upon substitution of ammonia by ethylenediamine. It was evident from the literature that *cis-α*-Co(trien)XClⁿ⁺ (X = Cl⁻, Br⁻ and RNH₂) reacts with Fe²⁺ via the chloride-bridged activated complex [42–45], so it is reasonable to assume a similar mechanism for our reactions. In such reactions of Co^{III} complexes, it had been suggested that the effect of a nonbridging *cis*-ligand on the rate is of minor importance [42, 43]. However, detailed information about the effect of the *cis*-ligand of the X was previously discussed in the literatures [42, 43]. The results for the *cis* isomer conform to those previously obtained in the reduction of Co(trien)XClⁿ⁺ (X = Cl⁻, Br⁻, RNH₂) by Fe^{II}, indicating that effect (b) was the important factor for variation in the rate. Moreover, in the case of the lower

alkylamine ligands from methylamine to butylamine [44], the reactivity successively decreases with an increase in the size of the amine ligand, but in the present study the reactivity increases suggesting that the formation of micelles by the complex itself catalyze the reaction. This suggests that the introduction of a higher long chain alkylamine group into the nonbridging *cis*-ligand facilitates the reaction rate. The presence of a higher long chain alkylamine group in the nonbridging ligand may stabilize the activated complex due to an increase in the solvation energy relative to that of the activated complex formed by the corresponding lower alkylamine ligand complex and Fe²⁺.

Temperature dependence

The temperature effect on (k) was studied at three different temperatures (303, 308 and 313 K) in order to obtain the thermodynamic parameters (Table 3) for the reaction between Co^{III} surfactant complexes and Fe²⁺.

From the transition state theory,

$$\ln(k/T) = \ln(k_B/h) + \Delta S^\ddagger/R - \Delta H^\ddagger/RT$$

the values of ΔS^\ddagger and ΔH^\ddagger were determined by plotting $\ln(k/T)$ versus $1/T$. From the slope, the value of ΔH^\ddagger was calculated ($-\Delta H^\ddagger/R$) and from the intercept $[\ln(k_B/h) + \Delta S^\ddagger/R]$ the value of ΔS^\ddagger was calculated. The values of entropy of activation (ΔS^\ddagger) and enthalpy of activation (ΔH^\ddagger) are given in Table 4. A meaningful mechanistic explanation was not possible, however as seen from the table the trends in the ΔH^\ddagger and ΔS^\ddagger values with increasing Co^{III} concentration were mainly due to the electrostatic attraction between the reductant and the oxidant micelle in the micellar phase. The ΔH^\ddagger obtained in this study was reasonable when compared to those values obtained for lower amines. ΔS^\ddagger shows that the transition state was well-structured in the micellar phase. The positive values of ΔS^\ddagger clearly indicate that the micellization was governed mainly by hydrophobic interactions between the surfactant cations, resulting in the breakdown of the structured water surrounding the hydrophobic groups, and indicates that the cationic surfactants were entropy driven processes.

Table 4. Thermodynamic parameters

Oxidizing agent	[Co ^{III}] × 10 ³ mol dm ⁻³	ΔH [‡] kJ mol ⁻¹	ΔS [‡] J K ⁻¹
<i>cis-α</i> -[Co(trien)(C ₁₆ H ₃₃ NH ₂)Cl] ²⁺	3.0	143.12	149.69
	4.0	158.86	203.97
	5.0	159.15	205.96
	6.0	157.17	201.23
	7.0	103.29	30.77
<i>cis-α</i> -[Co(trien)(C ₁₆ H ₃₃ NH ₂)Br] ²⁺	3.0	151.05	174.40
	4.0	170.35	239.78
	5.0	160.85	210.86
	6.0	155.55	195.38
	7.0	122.63	91.85

Binding mode of the coordinated halide ion, X^-

The trend: $F^- < Cl^- < Br^- < I^-$ was known as 'normal order' and the reverse was known as 'inverse order'. Several aspects related to the oxidant and reducing agents appear to be significant in determining the trend [43, 46]. $[Co(NH_3)_5X]^{2+}$ with Fe^{II} shows an inverse order [46], which may be treated according to the decreasing stabilities of FeX^{2+} in the order: $FeCl^{2+} > FeBr^{2+}$. It may be thus generalized that if the oxidant was a soft acid, one finds the inverse order and, if hard, normal order, the reductant in both cases being a hard acid. Hence, based on the above arguments one should expect an inverse trend for the Fe^{II} reduction of halogenocobalt(III)-complexes if the ET was mediated by bridging through the halide ion. In the present study, the ET was mediated by halide ion, Cl^-/Br^- and the trend was found to be in 'inverse order'.

We conclude that, the title reaction proceeds *via* an inner sphere pathway in aqueous solution and the formation of micelles by the title complex leads to alteration in the reaction rate.

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References

1. L. He, A. F. Dexter and A.P.J. Middelberg, *Chem. Eng. Sci.*, **61**, 989 (2006).
2. J.F. Galisteo, F.G. Santamaria, D. Golmayo, B. H. Juarez, C. Lopez and E. Palacios, *J. Opt. A: Pure Appl. Opt.*, **7**, S244 (2005).
3. C.L. Hill and X. Zhang, *Nature*, **373**, 324 (1995).
4. A. Corma, *Catal. Rev.:Sci. Eng.*, **46**, 3 (2004).
5. J.H. Fendler and E.J. Fendler, *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York, 1975.
6. C. Mavroidis, A. Dubey and M.L. Yarmush, *Ann. Biomed. Eng.*, **6**, 363 (2004).
7. V.V. Zhirnov and R.K. Cavin, *Nat. Mater.*, **5**, 11 (2006).
8. M. Schonhoff, *Curr. Opin. Colloid Interface Sci.*, **8**, 86 (2003).
9. M. Pisani, P. Bruni, C. Conti, E. Giorgini and O. Francescangeli, *Mol. Cryst. Liq. Cryst.*, **434**, 643 (2005).
10. K. Bernauer, S. Ghizdavu and L. Verardo, *Coord. Chem. Rev.*, **190**, 357 (1999).
11. M. Wolak, G. Stochel and R. Van Eldik, *J. Am. Chem. Soc.*, **125**, 1334 (2003).
12. V.O. Saik, A.A. Goun, J. Nanda, K. Shirota, H.L. Tavernier and M. D. Fayer, *J. Phys. Chem. A.*, **108**, 6696 (2004).
13. L. Burel, M. Mostafavi, S. Murata and M. Tachiya, *J. Phys. Chem. A.*, **103**, 5882 (1999).
14. H.L. Tavernier, A.V. Barzykin, M. Tachiya and M.D. Fayer, *J. Phys. Chem. B.*, **102**, 6078 (1998).
15. L. Hammarström, T. Norrby, G. Stenhagen, J. Martensson, B. Akermark and M. Almgren, *J. Phys. Chem. B.*, **101**, 7494 (1997).
16. S. Srinivasan, J. Annaraj and P.R. Athappan, *J. Inorg. Biochem.*, **99**, 876 (2005).
17. T.F. Tadros, *Applied Surfactants*, Wiley-VCH, Germany, 2005.
18. M. Islam, B. Saha and A.K. Das, *J. Mol. Catal. A: Chem.*, **236**, 260 (2005).
19. R. de la Vega, P. Perez-Tejeda, P. Lopez-Cornejo and F. Sanchez, *Langmuir*, **20**, 1558 (2004).
20. P. Lopez-Cornejo, P. Perez, F. Garcia, R. de la Vega and F. Sanchez, *J. Am. Chem. Soc.*, **124**, 5154 (2002).
21. R. Prado-Gotor, R. Jimenez, P. Perez-Tejeda, M. Lopez-Lopez and F. Sanchez, *Chem. Phys.*, **236**, 139 (2001).
22. R. Prado-Gotor, R. Jimenez, P. Lopez, P. Perez, C. Gomez-Herrera and F. Sanchez, *Langmuir*, **14**, 1539 (1998).
23. G.W. Walker, R.J. Geue, A.M. Sargeson and C.A. Behm, *J. Chem. Soc. Dalton Trans.*, **15**, 2992 (2003).
24. M. Iida, A. Sakamoto, T. Yamashita, K. Shundoh, S. Ohkawa and K. Yamanari, *Bull. Chem. Soc. Jpn.*, **73**, 2033 (2000).
25. D.M. Shah, K. M. Davies and A. Hussam, *Langmuir*, **13**, 4729 (1997).
26. G. Ghirlanda, P. Scrimin and L.A. Echegoyen, *Langmuir*, **12**, 5188 (1996).
27. A.M. Sargeson, *Coord. Chem. Rev.*, **151**, 89 (1996).
28. K.M. Davies, A. Hussam, B.R. Rector Jr., I. M. Owen and P. King, *Inorg. Chem.*, **33**, 1741 (1994).
29. D.P. Bendito and S. Rubio, *Trends Anal. Chem.*, **12**, 9 (1993).
30. T. Dwars, E. Paetzold and G. Oehme, *Angew. Chem. Int. Ed.*, **44**, 7174 (2005).
31. K. Santhakumar, N. Kumaraguru, S. Arunachalam and M.N. Arumugham, *Int. J. Chem. Kinet.*, **38**, 98 (2006).
32. K. Santhakumar, N. Kumaraguru, S. Arunachalam and M.N. Arumugham, *Transition Met. Chem.*, **31**, 62 (2006).
33. K. Santhakumar, N. Kumaraguru, M.N. Arumugham and S. Arunachalam, *Polyhedron*, In press.
34. M.N. Arumugam and S. Arunachalam, *Indian J. Chem.*, **36A**, 84 (1997).
35. S. Osinsky, I. Levitin, L. Bubnovskaya, A. Sigan, I. Ganusevich, A. Kovelskaya, N. Valkovskaya, L. Campanella and P. Wardman, *Exp. Oncol.*, **26**, 140 (2004).
36. C.A. Behm, I. Creaser, B. Daszkiewicz, R.J. Geue, A.M. Sargeson and G.W. Walker, *J. Chem. Soc. Chem. Commun.*, **24**, 1844 (1993).
37. C.A. Behm, P.F.L. Boreham, I.I. Creaser, B. Daszkiewicz, D.J. Maddalena, A.M. Sargeson and M. Snowdown, *Aust. J. Chem.*, **48**, 1009 (1995).
38. G. Ghirlanda, P. Scrimin, P. Tecillam and A. Toffoletti, *Langmuir*, **14**, 1646 (1998).
39. R.D. Cannon and J.J. Gardiner, *J. Chem. Soc. Dalton Trans.*, **89**, 887 (1972).
40. R.E. Kitson, *Anal. Chem.*, **22**, 664 (1950).
41. R.G. Linck, *Inorg. Chem.*, **9**, 2529 (1970).
42. P. Benson and A. Haim, *J. Am. Chem. Soc.*, **87**, 3826 (1965).
43. R.C. Patel and J.F. Endicott, *J. Am. Chem. Soc.*, **90**, 6364 (1968).
44. Y. Kurimura and K. Ohashi, *Bull. Chem. Soc. Jpn.*, **44**, 1797 (1971).
45. C. Bifano and R. G. Linck, *J. Am. Chem. Soc.*, **89**, 3945 (1967).
46. H. Diebler and H. Taube, *Inorg. Chem.*, **4**, 1029 (1965).