Factors controlling electron transfer reactions and stabilisation of uncommon oxidation states of chromium

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Abstract. Some experimental approaches to seek semi-quantitative understanding of factors controlling outer sphere electron transfer reactions of some transition metal complexes have been made. The relative importance of nuclear and electronic factors to outer sphere processes has been examined. By the manipulation of Franck–Condon or nuclear factors, it has now been possible to gain access into the chemistry of chromium in unusual oxidation states. An example of a reorganisation controlled electron transfer reaction involving Cr(IV)–Cr(III) system has been demonstrated. The bimolecular rate of reduction of diperoxoaquaethylenediamine chromium(IV) and diperoxodiethylenetriamine chromium(IV) is independent of the nature of th reductant employed viz. Fe^{2+} or VO^{2+} indicating that the generation of $\underline{6}$ coordinate Cr(IV) species from $\underline{7}$ coordinate of diperoxochromium(IV) reactant may be rate limiting. Similarly by increasing the barrier for the $\underline{6}$ coordinate to $\underline{4}$ coordinate structures through equatorial coordination of macrocyclic ligands, it has now been possible to detect through cyclic voltommogram the formation of relatively stable Cr(IV) species in the electrochemical oxidation of $Cr(Me_4[14]\ tetraene)(H_2O)_2^{3+}$ in aqueous sulphuric acid media. The kinetics and mechanism of the cerium(IV) and iodosyl benzene oxidation of $Cr(salen)(H_2O)_2^+$ and $Cr(salprn)(H_2O)_2^+$ have been investigated and kinetic and spectroscopic evidence for the formation of Cr(IV) transients and stable Cr(V) products has been presented. The relative importance of Franck–Condon factors in the oxidation of Cr(III) to Cr(IV) and Cr(V) states in different macrocyclic and multidentate ligand environments has been discussed.

Keywords. Cr(III)Schiff-bases; electron transfer; uncommon oxidation states; chromium(IV); chromium(V).

1. Introduction

Electron transfer and transport processes have attracted much attention in recent years (Isied 1990; Newton 1991; Weaver 1992). It is now recognised that electron transfer events can be attended also by changes in the molecular geometry and nuclear dispositions associated with the first coordination and solvent spheres (Weaver and McManis 1990 Weaver *et al* 1990; Tsukahara *et al* 1994). The contributions of donor–acceptor overlaps in promoting electron transfer events has formed an important area of study (Isied *et al* 1992; Siddarth and Marcus 1992). Especially in biological systems involving widely separated prosthetic groups, the precise understanding of factors regulating the long range electron transfer has evoked considerable interest (Beratan *et al* 1987; Isied *et al* 1992; Casimiro *et al* 1993).

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The relative contributions of Franck–Condon(nuclear) and electronic factors to outer sphere electron transfer processes have been discussed (Marcus 1982; Sutin 1983; Endicott *et al* 1983; Ramasami and Endicott 1984). Whereas Marcus type treatment of outer sphere processes have emphasised the contributions of nuclear factors neglecting the role of orbital overlap considerations, semi-empirical calculations of electron transfer probabilities in even simple systems like $Fe(H_2O_6)^{3+/2+}$ exchange indicate that donor acceptor orbital overlap is vital (Marcus 1982; Newton 1982; Tembe *et al* 1982; Ramasami and Endicott 1984).

2.   Experimental probes to factors controlling electron transfer reactivities

Experimental probes for detecting the contributions of electronic factors to outer sphere reactions have now been developed (Endicott and Ramasami 1982; Endicott *et al* 1983). Systematic studies have shown that in systems involving spin state and large bond length changes as well as widely separated donor–acceptor sites, the electron transfer probability within the activated complex can be less than unity (Sutin 1982; Ramasami and Endicott 1985; Endicott and Ramasami 1986). However, these studies have also shown that mixing of low lying excited state wave functions can well reduce the retardation factors to electron transfer in weakly coupled systems (Ramasami and Endicott 1985; Endicott and Ramasami 1986). The possible roles of the mixing of low lying charge transfer and ligand field excited states to reduce the non-adiabaticity of outer sphere electron transfer reactions have been discussed (Sutin 1982; Ramasami and Endicott 1985; Endicott and Ramasami 1986). A first order perturbation approach has been invoked which has been further treated (Newton and Sutin 1984). In this regard, it is of particular interest that the currently used models for explaining long range electron transfer processes in proteins tend to invoke coupling of donor–acceptor sites through even saturated peptide backbone (Isied 1984, 1991; Marcus and Sutin 1985; Winkler and Gray 1992). In principle, questions can be raised as to whether such high energy excited state wave functions can mix and perturb the electron transfer reaction coordinates to any significant extent. All these investigations seem to point out that even in weakly coupled donor–acceptor systems, there are several pathways which promote electron transfer events. However, the dominant role of Franck–Condon or nuclear factors in controlling redox processes has come to be recognized with due allowances for electronic only contributions. Taking advantage of the relatively dominant role played by Franck–Condon factors, it has now become possible to stabilise unusual oxidation states of metal ions and thereby gain access to the aqueous chemistry of some poorly characterized valence forms of metal ions (Gaslowitz and Taube 1981; Bixon and Jortner 1982; Nair *et al* 1987). In this work, some specific examples have been presented whereby the regulation of Franck–Condon factors to electron transfer processes, access to the aqueous chemistry of chromium in uncommon oxidation states has been gained.

3.   Status of the aqueous chemistry of chromium

The aqueous chemistry of chromium in di-, tri- and hexavalent states is well documented (Earley and Cannon 1965; Fackler and Holan 1965; Serpone *et al* 1983). On the other hand, the aqueous chemistry of chromium in tetra- and pentavalent states is less well defined. In the Frost diagram of chromium, figure 1, tetra- and pentavalent
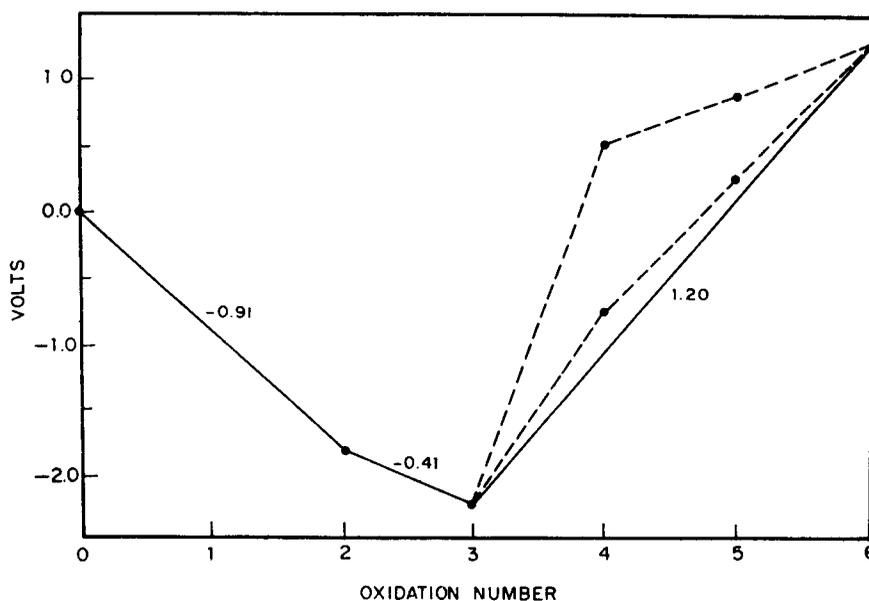
Figure 1. Frost diagram for chromium. The points for chromium(IV) and chromium(V) are estimated limits.

states are described as transients in several non-complementary reductions of chromium(VI). It is believed that chromium(VI) and (V) may resemble each other with respect to four coordinate and tetrahedral geometry and chromium(III) and (IV) may prefer six-coordinate and octahedral geometries as below (Edwards 1972).

$$\ce{Cr^{III} -> Cr^{IV} ->[r.d.s] Cr^{V} -> Cr^{VI}} \tag{1}$$
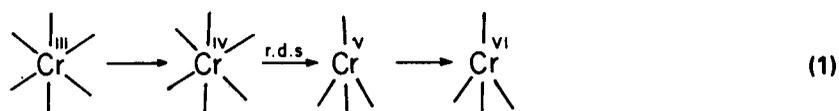
Some of the Cr(IV) and (V) complexes synthesised are associated with some unusual geometries and coordination numbers (Arshankow and Poznjak 1981; Srinivasan and Kochi 1985). Typically porphyrinato complexes of Cr(IV) and (V) have been prepared and characterized. In these complexes, the coordination geometry around the metal ion appears to be five-coordinate with distorted square-pyramid structure (Buchler et al 1982; Groves et al 1982, 1983). In recent years, there have been arguments that chromium-induced abnormalities in biological systems may well arise from the formation of chromium(V) and its implication with oxygen metabolism (Sugden et al 1991; Bose et al 1992; Sugiyama and Tsuzuki 1994). In this work, our efforts to probe the aqueous chemistry of chromium in tetra- and pentavalent states and some unresolved issues in the inorganic biochemistry of the metal ion during the last decade have been highlighted. As a strategy for the stabilisation of chromium in unusual oxidation states, namely (IV) and (V), the possible regulation of the nuclear reorganisational or Franck–Condon factors involved in redox interconversion of the metal ion has been examined.

4. Hypothesis made

If the generally believed hypothesis that Cr(IV) and Cr(III) prefer octahedral and Cr(VI) and Cr(V) tetrahedral geometries were true, it may be expected that Franck–Condon barriers for the interconversion of Cr(IV) and Cr(V) can be regulated by the choice of coordinated macrocyclic ligands. For instance, an equatorially coordinated macrocyclic ligand with some degree of unsaturation can be expected to render the interconversion of Cr(IV) and Cr(V) difficult because of the ring strain associated with the folding of equatorially coordinated macrocycles to take up tetrahedral geometries. In other words, the Franck–Condon barrier for Cr(IV)/(V) interconversion can be so enhanced that Cr(IV) and Cr(V) species with considerable life-times, may well be generated.

5. Stabilisation of chromium(IV) in aqueous media: The role of Franck–Condon factors

A series of chelate and macrocyclic complexes of chromium(III) have been synthesised with a view to generate Cr(IV) species with finite life-times using published procedures (Nair et al 1986; Kanthimathi et al 1995). The new complexes synthesised for this purpose are generally derived from tetraaza macrocyclic ligands with symmetrical [14]-membered intra-ligand ring size as shown in figure 2. It is generally believed that there may be a mismatch of intra-ligand cavity size and the radius of Cr(III) ion in the cases of tetraaza macrocycles bearing a symmetrical [14]-membered ring size. This raises a question as to whether such ligands with 14-membered ring can be advantageously employed to stabilise Cr(IV).
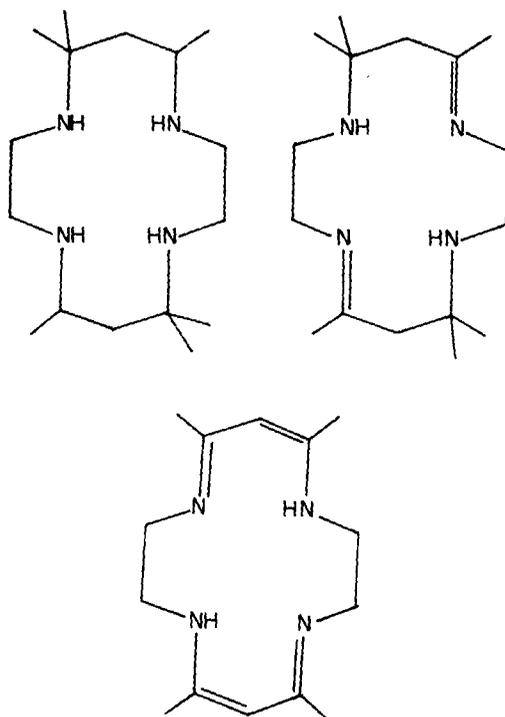

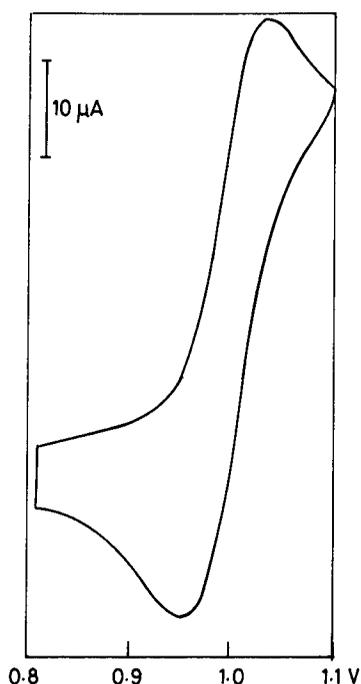**Figure 2.** Macrocyclic ligand with varying degrees of unsaturation.

Figure 3. The cyclic voltammogram of $Cr(Me_4[14]tetraene)(H_2O)_2^{3+}$ at $[H^+] = 2 \cdot 0\,M$, $I = 3 \cdot 0\,M$, scan rate $200\,mV/s$, $[Cr(III)] = 2 \cdot 5 \times 10^{-3}\,M$.

Our previous studies on the cerium(IV) oxidation of the $Cr(macrocycle)((H_2O)_2^{3+}$ (where macrocycle = Me_6-[14] ane (<u>1</u>), Me_6-[14] diene (<u>2</u>), Me_4-[14] tetraene (<u>3</u>) and cyclam (<u>4</u>)) have shown that the redox conversion of Cr(III) complexes into Cr(VI) is slow when a 14-membered unsaturated ligand like <u>3</u> is coordinated equatorially (Nair *et al* 1987). The kinetics of cerium(IV) oxidation of Cr(III) macrocyclic complexes have been reported already (Nair *et al* 1987). The main evidence for the stabilisation of Cr(IV) in the complex *trans*-$Cr(macrocycle)(H_2O)_2$ in aqueous sulphate medium has now been obtained through electrolytic oxidation. Cyclic voltammogram for the oxidation of <u>3</u> has been shown in figure 3. These studies on the oxidation of <u>3</u> in aqueous sulphuric acid medium provide convincing evidence for a single-electron step corresponding to the formation of a relatively stable Cr(IV) intermediate. That the electrochemical oxidation is nearly reversible with *E* separation of 60 mv suggests the redox process being nearly in the time scales of electrode reactions. In other words, the Cr(III)-(IV) couple in octahedral coordination geometries does not seem to implicate a large Franck–Condon barrier unlike in the case of several Cr(III)-(II) couples, which are electrochemically irreversible. This result is also further supported indirectly by a related study on the decomposition of chromium(IV) diperoxo complexes.

Diperoxoaquaethylenediamine chromium(IV) (<u>5</u>) and the related analogue diperoxodiethylenetriamine chromium(IV) (<u>6</u>) have been reported much earlier (Sriram *et al* 1979; Ranganathan *et al* 1986). Kinetic studies on the acid decomposition reactions of <u>5</u> and <u>6</u> investigated in our laboratory have shown that the protonation of peroxo units may make the 7-coordinate Cr(IV) complexes assume six-coordinate geometry; the conversion of Cr(IV) to Cr(III) in such a system is at least 10^8 times faster

Table 1. The bimolecular rate constants, k_r for the Fe(II) and V(IV) reactions with $Cr(O_2)_2 en(H_2O)$ and $Cr(O_2)_2(dien)$ when $I = 1.00$ M $(NaClO_4)$ and temperature $= 30°C$.

Ligand	Reductant	$k_r (M^{-1} s^{-1})$
Ethylene diamine	Fe(II)	$21 + 2$
Dien		$4.5 + 0.4$
Ethylene diamine	V(IV)	$38 + 6$
Dien		$4.5 + 2.6$
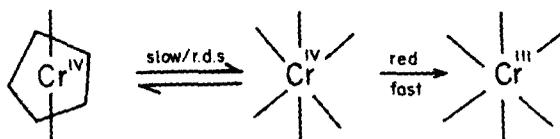
Scheme 1.

(Ranganathan et al 1986). An interesting observation on the role of reorganisational parameters in the interconversion of Cr(IV) and Cr(III) is in the kinetics of the reduction of 5 and 6 by $Fe(H_2O)_6^{2+}$ and VO^{2+}.

Bimolecular reduction of the seven-coordinate Cr(IV) diperoxo complexes by Fr(II) and V(IV) has been investigated. Rate constants for the outer sphere reduction of the Cr(IV) complexes by Fe(II) and V(IV) are expected to vary by a factor of 40 because of the differences in the oxidation potentials of Fe(II)/(III) and V(IV)/V(V) couples, if the redox reaction is electron-transfer controlled. The observed bimolecular rate constants for the Fe(II) and V(IV) reduction of 5 and 6 are as given in table 1. Identical rate constants are predicted for Fe(II) and V(IV) reductions if the overall reaction is controlled by geometry or other conformational changes in Cr(IV) complexes prior to electron transfer event as in scheme 1. It is tempting to propose that the reduction of seven-coordinate Cr(IV) diperoxo complexes by Fe(II) and V(IV) may be limited by the intramolecular conversion of pentagonal bipyramid geometry into an octahedron. The relatively slow conversion of Cr(IV) diperoxo complexes into Cr(III) may well be ascribed to large changes in the geometries. On the basis of the nearly identical rate constants for the Fe(II) and V(IV) reduction of the diperoxo complexes, a reaction scheme in which the reorganisation rather than electron transfer controls the rate process has now been invoked.

6. Stabilisation of the chromium(V) oxidation state

Although a limited number of Cr(V) complexes has already been reported (Arshankow and Poznjak 1981; Groves et al 1982, 1983; Srinivasan and Kochi 1985) and characterized, directed synthesis of chromium(V) complexes has been difficult. It has now been possible in this study to oxidise a series of $Cr(Schiff\ base)(H_2O)_2^+$ complexes by cerium(IV), iodosyl benzene and hypochlorite and generate relatively stable Cr(V) complexes of the general formulation $O=Cr(Schiff\ base)^+$. The nature of the products

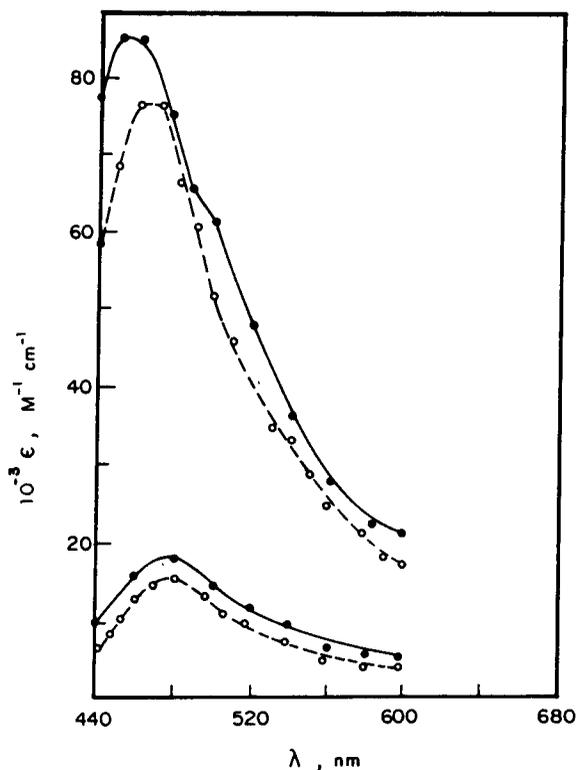**Figure 4.** Visible spectra of bluish intermediate of $Cr(salprn)(H_2O)_2^+$ (————) $Cr(salen)(H_2O)_2^+$ (— — — —) and final reaction product of $Cr(salprn)(H_2O)_2^+$ (————) and $Cr(salen)(H_2O)_2^+$ (— — — —) in the Ce(IV) oxidation of $Cr(Schiff-base)(H_2O)_2^+$ complexes at $[H^+] = 0.4$ M, $I = 1.0$ M $(LiClO_4)$, $[SO_4^{2-}] = 0.1$ M and $T = 25°C$.

formed from the oxidation given in (2) has been analysed,

$$trans\text{-}Cr(Schiff\ base)(H_2O)_2^+ + oxidants \rightarrow products, \tag{2}$$

where Schiff base = 1,2- *bis*(salicylidineamino)ethane (salen), 7 and 1,3-*bis*(salicyli-dineamino)propane (salprn), 8 and oxidants are Ce(IV), OIC_6H_5, and NaClO.

At the end of reaction given in (2), the chromium products could be isolated in solid state when the oxidant is iodosyl benzene. In the case of Ce(IV) oxidation, transient spectra could be obtained. A two-stage process with a build up of a blue intermediate which underwent decay to a brown coloured end product could be observed. The stopped flow spectra of the blue intermediate and brown end products are as shown in figure 4. The reaction stoichiometry for each stage has been investigated for the Ce(IV) oxidation of the Schiff base complexes, 7 and 8. The first stage exhibits a Cr(III):Ce(IV) stoichiometry of 1:1 and the second stage 1:2 respectively within experimental error. On the basis of the available experimental data, the Ce(IV) oxidation of 7 and 8 could be written as below,

$$trans\text{-}Cr(Schiff\ base)(H_2O)_2^+ + Ce(IV) \rightarrow Cr(IV) + Ce(III), \tag{3}$$

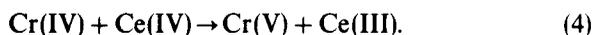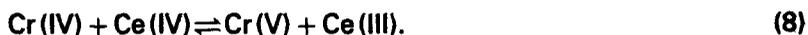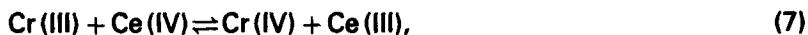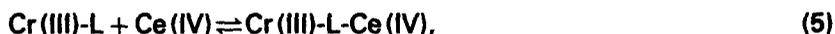$$Cr(IV) + Ce(IV) \rightarrow Cr(V) + Ce(III). \tag{4}$$

Table 2. The observed rate constants data for the first and second stages, k_f and k_s for the Ce(IV) oxidation of $Cr(salprn)(H_2O)_2^+$ at $[Cr(III)] = 0.5 \times 10^{-4}$ M; $I = 1.0$ M, $[H^+] = 0.4$ M; $[Ce(III)] = 1 \times 10^{-4}$ M and $T = 25°$C.

λ(nm)	$10^2[SO_4^{2-}]$(M)	$10^3[Ce(IV)]$(M)	$k_f(s^{-1})$	$k_s(s^{-1})$
560	6.0	0.5	0.69	0.14
	6.0	1.0	1.35	0.19
	6.0	1.5	1.85	0.30
	6.0	2.0	2.10	0.49
	6.0	2.5	2.31	0.58
	6.0	3.25	3.25	0.66
	6.0	4.0	3.65	0.62
416	6.0	0.5	0.67	0.14
	6.0	1.0	1.40	0.18
	6.0	1.5	1.82	0.29
	6.0	2.0	2.09	0.48
	6.0	2.5	2.31	0.59
	6.0	3.25	3.20	0.65
	6.0	4.0	3.68	0.66
560	3.0	1.0	2.81	0.16
	4.0	1.0	2.10	0.17
	6.0	1.0	1.99	0.16
	8.0	1.0	1.71	0.16
	10.0	1.0	1.62	0.11
	12.0	1.0	1.27	0.12

Flow ESR experiments have helped to establish the oxidation state of the chromium product at the end of the reaction given in (4), but the precise structure of the species has not yet been established (Nair *et al* 1994).

The kinetics of the overall oxidation of *trans*-$Cr(Schiff\ base)(H_2O)_2^+$, where Schiff base = salen or salprn, by Ce(IV) have now been investigated. Two-stage kinetics with well-separated half-lives have been observed for the pseudo first-order oxidation of the Cr(III) species by Ce(IV). The kinetic data obtained from stopped flow techniques for the two-stage oxidation are given in table 2. The observed rate constants for the first stage which is formally assigned to the formation of Cr(IV) intermediate as in (3) is designated as k_f and the second stage corresponding to the formation of the Cr(V) product is denoted as k_s. The observed rate constants, k_f, exhibit a less than first-order dependence on [Ce(IV)] as in figure 5. The plot of $\{k_f\}^{-1}$ against $[Ce(IV)]^{-1}$ is linear with a positive intercept. These data can be easily rationalized in terms of a reaction (scheme 2) in which a preequilibrium of Ce(IV) and Cr(III) complex is achieved prior to an intra molecular electron-transfer step.

$$Cr(III)\text{-}L + Ce(IV) \rightleftharpoons Cr(III)\text{-}L\text{-}Ce(IV), \tag{5}$$

$$Cr(III)\text{-}L\text{-}Ce(IV) \rightarrow Cr(IV)\text{-}L + Ce(III), \tag{6}$$

$$Cr(III) + Ce(IV) \rightleftharpoons Cr(IV) + Ce(III), \tag{7}$$

$$Cr(IV) + Ce(IV) \rightleftharpoons Cr(V) + Ce(III). \tag{8}$$

Scheme 2.
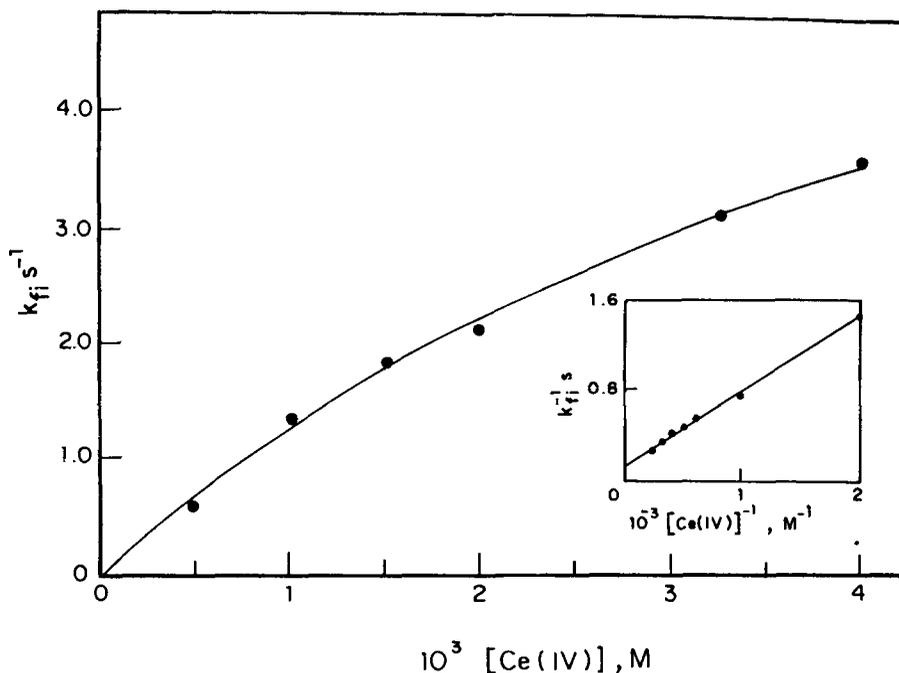
Figure 5. Plot of k_f against [Ce(IV)] for the reaction of $Cr(Salprn)(H_2O)_2^+$ with Ce(IV) at $[Cr(III)] = 1 \times 10^{-4}\,M$, $I = 1.0\,M$ (LiClO$_4$), $[H^+] = 0.4\,M$, $[SO_4^{2-}] = 0.1\,M$, $T = 25°C$ and $\lambda = 560\,nm$.

The observed rate constants for the second stage k_s, exhibit a precise first-order dependence on [Ce(IV)]. In other words, the oxidation of Cr(IV) by Ce(IV) follows a bimolecular rate law, establishing an irreversible chemical reaction. This is of particular interest. In the case of the non-complementary oxidation of $Cr(H_2O)_6^{3+}$ and related complexes by Ce(IV), it has been established that the Cr(IV)/Cr(V) or Cr(VI) potentials need to be higher than that of Ce(IV)/Ce(III) couples; because the overall reaction is retarded by added Ce(III). A reversible equilibrium as in (7) and (8) has been invoked for explaining the kinetic data in previous studies. In the present study, it is established that Cr(III)/Cr(IV) as well as Cr(IV)/Cr(V) potentials need to be less than that of Ce(IV)/Ce(III) redox couple on the basis of lack of retardation of oxidation by added [Ce(III)]. In other words, the chelation of Cr(III) to the Schiff bases, salen or salprn may lower the redox potentials of Cr(III)/Cr(IV) as well as Cr(III)/Cr(V) couples. Attempts to measure directly the redox potentials for the Cr(III)/(IV) as well as Cr(III)/(V) couples have not been successful so far in the ligand environment chosen, due to the electrochemical irreversibility of the redox step. It has been established that the coordination environment around Cr(III) in 7 is distorted with chromium atom lying above the plane of the ring donor atoms and in 8 a more regular octahedral arrangement is realized (Coggon *et al* 1970; Kanthimathi *et al* 1995).

If the coordination geometries of the Cr(V)-oxo products resulting from the oxidations of 7 and 8 varied significantly, a substantial difference in the rate of oxidation by Ce(IV) may be expected. However, the ratio of the bimolecular rate of oxidation of 7 and 8 by Ce(IV) is 2:2:1. In other words, the Franck–Condon factors

Table 3. The pseudo first order rate constants k_i for the reaction of iodosyl benzene (IB) with Cr(Schiff-base) $(H_2O)_2^+$ at $[Cr(III)] = 0.5 \times 10^{-4}$ M, $[H^+] = 0.01$ M, $I = 0.05$ M (LiClO$_4$) $T = 30°C$ and $\lambda = 590$ nm.

Schiff-base	$10^3[IB]$(M)	$10^3 k_i$(s^{-1})
	0·65	1·6
Salen	1·30	3·8
	1·95	5·5
	0·70	9·9
Salprn	1·10	13·9
	1·40	18·0
	2·10	28·9

involved in the Ce(IV) oxidation of 7 and 8 by Ce(IV) appear to be similar. This trend is observed not only in the inner sphere oxidation of the Cr(III)-Schiff base complexes 7 and 8 by Ce(IV) but also in the oxygen transfer reaction of the same Cr(III) species with iodosyl benzene.

The kinetics of the oxidation of 7 and 8 by iodosyl benzene have been investigated. The observed pseudo first-order rate constants k_i are listed in table 3 for both the complexes. The bimolecular rate constants k_b for the iodosyl benzene oxidation of 7 and 8 are 2·9 and 13·0 M^{-1}s^{-1}, respectively. The small differences in the geometrical parameters around the coordination environment around Cr(III) in the Schiff base complexes 7 and 8 do not seem to influence the oxygen atom transfer process with iodosyl benzene to form the oxo cations O=Cr(Schiff base)$^+$ significantly.

7. Conclusions

It has now been possible to factorize the various contributions to electron transfer reactivities in transition metal complexes as related to Franck–Condon and electronic factors. However, there still remain a number of unresolved issues in long-range electron transfer events that call for a more complete understanding of the possible role of peptide units in facilitating donor–acceptor orbital mixing. For the treatment of outer sphere processes, experimental probes to electronic factor contributions as well as semi-quantitative treatment have emerged. Quantitative understanding of factors controlling fundamental electron-transfer steps seems to enable us to gain insight into the aqueous chemistry of metal ions in hitherto less-defined oxidation states. Such insights may help in assessing the potential roles of uncommon oxidation states of metal ions in real life systems. For instance, the potential biofunctions of Cr (V) and Cr(IV) can now be understood more completely by taking recourse to the directed synthesis of such compounds. Our recent studies on Cr(V) species generated from 7 and 8 show that they may well be implicated in the metal ion-induced apoptosis (programmed death) of human lymphocyte cells (Rajaram *et al* 1995).

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