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The reactions of transition metal ions with chlorine(III)

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Contents

Abstract

Practical applications and unique kinetic phenomena have generated considerable interest in the redox chemistry of chlorine(III). The complex kinetic and stoichiometric features of the related reactions are well documented, but relatively little is known about possible interactions between chlorine(III) and transition metal ions. Recent studies confirmed that the chlorite ion forms weak complexes with common metal ions such as Cu(II), Fe(III) or Hg(II) and the formation of an inert chlorito complex was also reported. This paper reviews kinetic and equilibrium aspects of the formation of chlorito complexes as well as the role of

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transition metal ions in the redox reactions and the catalytic decomposition of chlorine(III). It will be shown that the metal ions enhance the reactivity of chlorine(III) by activating the O–Cl bond. Chlorito complexes may undergo either redox decomposition or promote the reactions of the coordinated chlorine(III) with other oxychlorine species. It is a common feature that reactive intermediates are formed, which are involved in subsequent fast reactions with the reactants and other intermediates. As a consequence, complex kinetic patterns ensue and the stoichiometries are kinetically controlled. Mechanistic aspects of these reactions will be discussed in detail.

Keywords: Chlorite ion; Oxychlorine species; Chlorito complexes; Transition metal complexes; Redox reactions; Electron transfer; Autocatalysis

1. Introduction

Chlorine exists in various oxidation states from -1 to $+7$ in aqueous solution [1]. Chlorite ion/chlorous acid,[1] with chlorine in the $+3$ oxidation state, is in the middle of this series and can be involved in a redox process as either an oxidizing or a reducing agent. Reactions with strong oxidants produce chlorine dioxide and/or chlorate ion. The reduction of chlorite ion typically yields chloride ion as the main product.

In practical applications, chlorine(III) is often used as a disinfectant, mild oxidant or a precursor in the generation of chlorine dioxide [2–9]. In the presence of appropriate catalysts, such as the (salen)manganese(III) complex, ClO_2^- is an efficient agent for regioselective chlorination [10,11]. The specific kinetic features observed in the reactions of chlorine(III) have also been the subject of intense study. In any reaction which involves the reduction of Cl(III) to Cl^-, four electrons are transferred to the oxidant. This cannot occur in a concerted step and the overall reaction progresses through the formation of reactive intermediates. Under specific conditions, the kinetic coupling between the competing reaction paths is the source of unique kinetic phenomena such as clock reaction, periodic oscillation, chaotic behavior, etc. [12–16].

While chlorite ion is stable in alkaline solution, it decomposes in an acid catalyzed reaction into chlorate ion, chlorine dioxide and chloride ion [17]. The stoichiometry and kinetics of the decomposition are sensitive to the conditions applied. Neutral aqueous solutions of chlorine(III) are reasonably stable in the dark, but impurities may significantly reduce the lifetime. This phenomenon can be assigned to the presence of trace amounts of transition metal ions, presumably mainly to iron(III), which may also significantly affect the kinetic patterns in the redox reactions of chlorite ion. Nevertheless, only limited information is available for the reactions of chlorine(III) with transition metal ions. Literature data are

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[1] Chlorite ion and chlorous acid are in fast protolytic equilibrium and their concentration ratio is determined by the pH. In this paper, the two species will not be distinguished unless it is required by the clarity of presentation.

available for a few redox reactions, and until recently little was known about chlorite ion as a ligand. In the present paper, a survey is given of the complex formation and redox reactions of chlorite ion with transition metal ions. It will be shown that coordination of ClO_2^- to the metal center is in the core of the mechanisms of the corresponding redox processes.

2. The protonation constant of ClO_2^-

Acid–base equilibrium between chlorite ion and chlorous acid plays an important role in the aqueous chemistry of chlorine(III), and quantitative interpretation of the pH-dependent phenomena requires the exact knowledge of the protonation constant. The equilibrium constant for reaction (1) was determined by using a variety of experimental methods

$$ClO_2^- + H^+ \rightleftharpoons HClO_2 \tag{1}$$

$$K_p = \frac{[HClO_2]}{[H^+][ClO_2^-]}$$

The literature values for log K_p are in the range of 1.3–2.3 [18–26]. The relatively large variation in K_p is probably due to the interference of acid catalyzed disproportionation of chlorous acid [27,28] with the equilibrium measurements. The actual stoichiometry of the decomposition is sensitive to the conditions applied and can be given by the combination of the following two equations [27]:

$$4HClO_2 = 2ClO_2 + ClO_3^- + Cl^- + 2H^+ + H_2O \tag{2}$$

$$5HClO_2 = 4ClO_2 + Cl^- + H^+ + 2H_2O \tag{3}$$

Although this reaction is not particularly fast [29], steady generation of the strongly absorbing chlorine dioxide, $\varepsilon = 1250\ M^{-1}\ cm^{-1}$ at $\lambda_{max} = 358.5$ nm [27],[2] may have significant contribution to the spectra in conventional spectrophotometric studies. Thus, evaluation of the spectral data could lead to falsified values for K_p whenever the decomposition of chlorine(III) was neglected. The decomposition could also produce considerable amounts of free proton while the electrode equilibrium was attained in pH-metric measurements. This could result in biased pH readings. The effects of the side reactions were minimized in combined stopped flow–rapid scan spectrophotometric experiments [24]. The spectra were taken as the average of several scans within 100–200 ms after mixing an aqueous solution of chlorite ion with perchloric acid in increasing concentrations (Fig. 1). The lack of measurable absorbance at the 360 nm maximum of chlorine dioxide is a clear indication that the decomposition of chlorite ion is negligible within this time frame. Consequently, these data probably yielded one of the most reliable values for K_p. On the basis of the pH dependence of the spectra, log $K_p = 1.72$ ($I = 1.0$ M $NaClO_4$, 25°C).

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[2] The maximum absorbance of chlorine dioxide is quite often quoted at 360 nm instead of 358.5 nm in the literature.

3. The coordination chemistry of chlorine(III)

3.1. The chloritopentaamminecobalt(III) complex

So far, the only kinetically inert complex of chlorite ion, $(NH_3)_5Co(ClO_2)^{2+}$, was reported by Thompson in 1979 [30]. This species was prepared by introducing a vigorous stream of ClO_2 into a constantly stirred and cooled solution of $Co(NO_3)_2$ in ammonium nitrate–ammonia buffer. After precipitation as fine reddish crystals, the complex was purified by crystallization from dilute nitric acid. The synthesis was made in the dark in order to avoid photodecomposition. The complex appeared to be stable for an extended period of time in the absence of light. Characteristic absorbance maxima for $(NH_3)_5Co(ClO_2)^{2+}$ were reported at 358 and 515 nm with molar absorptivities of 2320 and 87 $M^{-1}\,cm^{-1}$, respectively.

While the X-ray structure of the nitrate salt of the complex could not be determined, recently an appropriate compound could be prepared for structural studies with $[Pd(CN)_4]^{2-}$as a counter ion [31]. The red $[(NH_3)_5Co(ClO_2)][Pd(CN)_4]\cdot H_2O$ salt forms triclinic, $P1$, crystals with the following lattice parameters: $a = 719.92$, $b = 948.73$, $c = 1177.52$ pm, $\alpha = 66.680$, $\beta = 75.784$, $\gamma = 82.203°$ and $Z = 2$ giving a cell volume of 7.1527×10^{-22} cm^3. The structure of the chlorito complex is shown in Fig. 2. According to these results, the chlorite ion is O-bonded in the complex and the Co–O–Cl angle, 122.1°, strongly suggests that an sp^3 hybrid electron pair is involved in the coordination. An analysis of the crystallographic data reveals that the coordination to the metal center lengthens the O–Cl bond adjacent to Co^{3+}. As will be discussed in Section 4.1, this feature is consistent with the kinetic behavior of the complex in redox processes and explains the observed differences in the reactions of free and coordinated chlorite ions.

The $(NH_3)_5Co(ClO_2)^{2+}$ complex slowly decomposes in acidic solution [30]. The intramolecular redox process produces chlorine dioxide and cobalt(II) in equal

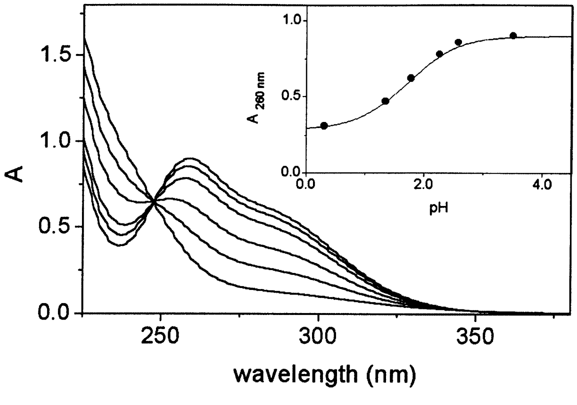

Fig. 1. The spectrum of chlorine(III) as a function of acidity. [Cl(III)] = 6.22×10^{-3} M; $[H^+]_{tot} = 0$, 3.46×10^{-3}, 6.92×10^{-3}, 1.98×10^{-2}, 4.94×10^{-2} and 0.494 M in the order of decreasing absorbance at 260 nm; 1.0 M $NaClO_4$, 25.0°C. Inset: the absorbance at 260 nm as a function of pH [24].

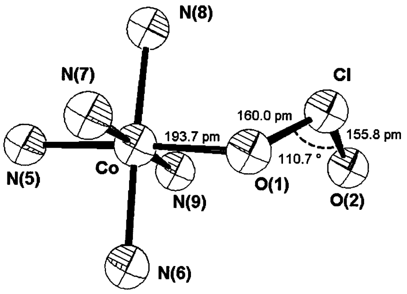

Fig. 2. The X-ray structure of the $[(NH_3)_5Co(ClO_2)]^{2+}$ complex [31].

amounts but the formation of trace amounts of $(NH_3)_5Co(H_2O)^{3+}$ was also observed. The reaction follows strictly first-order kinetics and the stoichiometry can be approximated as follows:

$$(NH_3)_5Co(ClO_2)^{2+} + 5H^+ = 5NH_4^+ + Co^{2+} + ClO_2 \qquad (4)$$

The decomposition rate is independent of pH, and evidence for the formation of a partially aquated Co(III) intermediate was not found. The rate constant for the decomposition at 50°C and the activation parameters are 2.6×10^{-4} s^{-1}, $H^‡ =$ 105.9 kJ mol^{-1} and $S^‡ = 12.6$ J mol^{-1} K^{-1}, respectively. The observations led to the conclusion that the rate-determining step of the reaction is an internal electron transfer from the chlorite ligand to the Co(III) center.

3.2. Chlorito complexes with labile transition metal ions

The existence of labile chlorito complexes was postulated in several redox reactions of the chlorite ion. Direct experimental evidence for the formation of such species was first reported by Gordon and Kern [32]. These authors observed a transient yellow color in the oxidation of uranium(IV) by the chlorite ion. The analysis of this phenomenon led to the conclusion that this spectral effect is due to the formation of an uranyl(VI) chlorito complex.[3] Because a weak complex is formed, small absorbance changes were observed even at relatively high concentrations of the reactants and only a lower limit could be estimated for the stability constant.

The spectral effects were much better defined in the reactions of chlorite ion with copper(II) [24] and mercury(II) [33]. Immediately after mixing the reactants, new absorbance maxima appeared in the spectra, which could not be assigned to any known component (metal ions, chlorite ion and chlorine dioxide) in the corresponding reaction mixtures (Fig. 3). In the case of copper(II), the intense yellow color strongly resembled the color of ClO_2. However, the very intense odor of chlorine

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[3] For the sake of simplicity, coordinated water molecules are not shown in the formulae of the complexes.

dioxide was absent from the samples and spectrophotometric measurements clearly showed distinct features of the spectra. The strong molar absorptivities at the characteristic absorbance maxima (Table 1) seem to be consistent with a ligand-to-metal charge transfer band in both complexes.

The properties of these complexes are quite different with respect to redox reactions. While aqueous solutions of $CuClO_2^+$ appear to be stable for an extended period of time [24], the $HgClO_2^+$ complex is involved in unique kinetic phenomena in the mercury(II)–chlorite ion–chlorine dioxide system (cf. Section 4.3) [33]. In order to avoid spectral interferences from side reactions, which generate ClO_2, the complex formation reactions were studied using the stopped-flow technique. Ligand substitution reactions of Cu(II) and Hg(II) with simple ligands are typically diffusion controlled and, as expected, the complexes formed within the dead-time of the stopped-flow measurements (1–2 ms). These studies revealed that the side reactions and the spectral effects of ClO_2 formation could be neglected up to several hundred milliseconds after mixing the reactants.

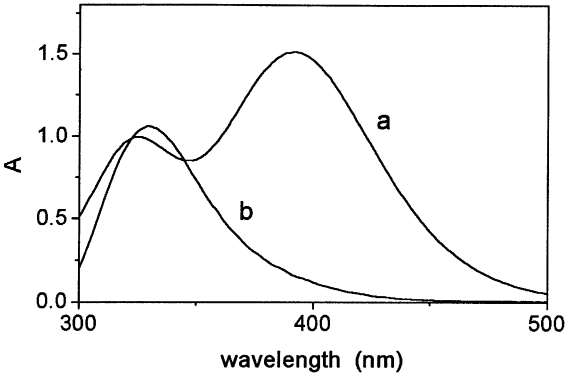


Fig. 3. The spectra of $CuClO_2^+$ (a) and $HgClO_2^+$ (b). a: $[Cu^{2+}]_{tot} = 3.0 \times 10^{-2}$, $[Cl(III)]_{tot} = 2.0 \times 10^{-2}$, and $[H^+] = 1.5 \times 10^{-3}$ M; b: $[Hg^{2+}]_{tot} = 1.5 \times 10^{-2}$, $[Cl(III)]_{tot} = 5.0 \times 10^{-3}$, and $[H^+] = 2.5 \times 10^{-2}$ M.

Table 1
Equilibrium constants and molar absorbencies for chlorito complexes (1.0 M $NaClO_4$; 25.0°C)

Complex	K (M^{-1})	λ (nm)	ε (M^{-1} cm^{-1})	Ref.
$UO_2ClO_2^+$	>0.02	370	5.0×10^3 [a]	[32]
$CuClO_2^+$	1.04	387 [b]	1990	[24]
$FeClO_2^{2+}$	13.8	510	636	[34]
	13.2 [c]			[25]
$HgClO_2^+$	41.7	325 [b]	727	[33]

[a] $K\varepsilon$.

[b] Wavelength of maximum absorbance.

[c] 5.0°C.

The concentration dependencies of the spectra obtained from the initial phase of the reactions, and detailed studies using Job's method confirmed the formation of 1:1 complexes:

$$M^{2+} + ClO_2^- \rightleftharpoons MClO_2^+ \quad (M^{2+} = Cu^{2+}, Hg^{2+}) \tag{5}$$

$$K_M = \frac{[MClO_2^+]}{[M^{2+}][ClO_2^-]}$$

The stability constants and molar absorptivities at the characteristic absorbance maximum of the complexes are listed in Table 1.

The existence of another complex was confirmed in the iron(III)–chlorite ion system [34]. When solutions of iron(III) and chlorite ion were mixed, a steady absorbance increase at around 360 nm was consistent with the formation of chlorine dioxide. However, the unexpectedly high absorbance and the distinctly different kinetic features above 470 nm clearly indicated the formation of a new species. In this wavelength range, the absorbance reached a steady value within 50 ms and either increased or decayed only toward the end of the overall reaction, which typically lasted for several hours or even a day. A comparison of the results obtained in the absence and presence of iron(III) strongly suggests that catalytic decomposition of the chlorite ion and the formation of the chlorito complex occur simultaneously (cf. Section 4.3) [35]. Because of strong overlap between the spectra of the complex and the product chlorine dioxide, the equilibrium and kinetics of the complex formation could be studied independently only above 500 nm. Typical stopped-flow traces at 510 nm were consistent with a fast first-order process. The final absorbances at 40–50 ms, A_∞, and the pseudo-first-order rate constants, k_{obs}, were interpreted by considering reactions (2), (6) and (7):

$$Fe^{3+} + ClO_2^- \rightleftharpoons FeClO_2^{2+} \tag{6}$$

$$K_{Fe} = \frac{[FeClO_2^{2+}]}{[Fe^{3+}][ClO_2^-]}$$

$$Fe^{3+} \rightleftharpoons Fe(OH)^{2+} + H^+ \tag{7}$$

$$K_h = \frac{[Fe(OH)^{2+}][H^+]}{[Fe^{3+}]}$$

Under the conditions applied, $[Fe(III)]_{tot} < 1.1 \times 10^{-3}$ M and pH < 2.1, the formation of other hydroxo complexes could be rejected from the equilibrium model. Provided that the only absorbing species is the chlorito complex at 510 nm and the chlorite ion is always in large excess over iron(III), the following expression applies to A_∞:

$$A_\infty = \frac{K'_{Fe}C_{Cl(III)}}{1 + K'_{Fe}C_{Cl(III)}} \varepsilon C_{Fe(III)} \tag{8}$$

where

$$K'_{\mathrm{Fe}} = \frac{K_{\mathrm{Fe}}}{(1 + (K_{\mathrm{h}}/[\mathrm{H}^+]))(1 + K_{\mathrm{p}}[\mathrm{H}^+])}$$

and $C_{\mathrm{Cl(III)}}$, $C_{\mathrm{Fe(III)}}$ stand for the total concentrations of the corresponding components. This model gave excellent fit of the experimental data. The stability constants and the molar absorptivity reported for the $\mathrm{FeClO_2^{2+}}$ complex are listed in Table 1.

In the most general case, ligand substitution reactions may involve the metal ion, its hydroxo complexes and both the protonated and unprotonated forms of the ligand. Therefore, the following pathways were considered for the formation of the chlorito complex:

$$\mathrm{Fe^{3+} + ClO_2^- \rightleftharpoons FeClO_2^{2+}} \quad k_{6a}, k_{-6a} \tag{6a}$$

$$\mathrm{Fe(OH)^{2+} + HClO_2 \rightleftharpoons FeClO_2^{2+}(+H_2O)} \quad k_{6b}, k_{-6b} \tag{6b}$$

$$\mathrm{Fe^{3+} + HClO_2^- \rightleftharpoons FeClO_2^{2+} + H^+} \quad k_9, k_{-9} \tag{9}$$

$$\mathrm{Fe(OH)^{2+} + ClO_2^- \rightleftharpoons Fe(OH)ClO_2^+} \quad k_{10}, k_{-10} \tag{10}$$

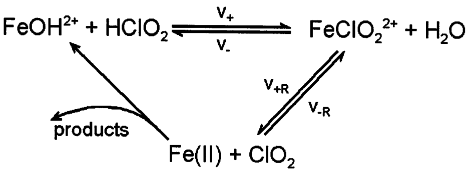
$$\mathrm{Fe(OH)ClO_2^+ + H^+ \rightleftharpoons FeClO_2^{2+}(+H_2O)} \tag{11}$$

On the basis of the pH dependence of k_{obs}, reaction (9) could be excluded from the model. The interpretation of the kinetic data under ambient conditions (25°C and 1 bar) was somewhat ambiguous. However, the results at 5°C confirmed that reactions (10) and (11) can also be rejected from the model [25]. It was shown that the formation of the $\mathrm{FeClO_2^{2+}}$ complex is kinetically coupled with its redox decomposition as demonstrated in Scheme 1 [35]. The decomposition proceeds via a reactive transient species and regenerates iron(III). Because the intermediate is in steady state, a simple second-order kinetics is observed but the redox path increases the apparent dissociation rate of the complex. According to a detailed analysis of the data, the rate of the redox decomposition is inversely proportional to $[\mathrm{H}^+]$. By considering that the hydrolysis of iron(III) (reaction (7)) and the protonation of the ligand (reaction (2)) are fast pre-equilibria, the following expression can be derived for k_{obs}:

$$k_{\mathrm{obs}} = \left(QC_{\mathrm{Cl(III)}} + \frac{1}{K_{\mathrm{Fe}}}\right)(k_{6a} + k_{6b}K_{\mathrm{p}}K_{\mathrm{h}}) + \frac{k_{\mathrm{r}}}{[\mathrm{H}^+]} \tag{12}$$

where

$$Q = \frac{[\mathrm{H}^+]}{([\mathrm{H}^+] + K_{\mathrm{h}})(1 + K_{\mathrm{p}}[\mathrm{H}^+])}$$



Scheme 1.

and k_r is the apparent rate constant for the redox decomposition [25].

As long as the protolytic reactions are fast pre-equilibria, reaction (6a) and the conjugate acid–conjugate base, CACB, path (6b) are indistinguishable under ambient conditions. Mechanistic details of the complex formation were evaluated on the basis of pressure dependent studies up to 1250 bar at 5°C [25]. The volume of activation for the formation of the chlorito complex, $V^{\ddagger} = +6.9$ cm^3 mol^{-1}, is practically the same as for the water exchange reaction on $Fe(H_2O)_5OH^{2+}$, $V^{\ddagger} = +7.0$ cm^3 mol^{-1} [36]. The excellent agreement of these data implies that both reactions proceed via the same dissociative interchange mechanism (I_d), i.e. the CACB path is operative in the formation of the chlorito complex. In this mechanism, the coordination of the ligand is preceded by the rate-determining dissociation of a coordinated water molecule from the hydroxo complex. Presumably, the process is completed by a fast intramolecular proton-transfer step between the reactants. A comparison of the results with volumes of activation for other ligand substitution reactions of iron(III) indicates that the mechanism of these reactions are controlled by the nucleophilic strength of the entering ligand. Ligands of high nucleophilicity are able to penetrate the primary coordination sphere of the metal center and react with $Fe(H_2O)_6^{3+}$ via an associative interchange mechanism (I_a). In contrast, weak nucleophiles, such as chlorite ion, react with $Fe(H_2O)_5(OH)^{2+}$ through an I_d activation [25].

According to the data in Table 1, mercury(II) forms a more stable complex with chlorite ion than iron(III) and copper(II). However, simple electrostatic considerations would predict the Fe(III) > Cu(II) ~ Hg(II) stability order. (Because of the noted ambiguity in the stability constant of UO_2^{2+}, the chlorito complex of this ion is not involved in the comparison.) The unexpected trend in the stability constants was interpreted in terms of the hard–soft character of the metal ions by considering that chlorite ion may be coordinated to the metal center via either an oxygen atom or the chlorine atom [33]. While in the case of the hard iron(III) and copper(II) probably the O-coordination is preferred, the Cl-coordination is expected to be favorable with the soft mercury(II). As an analogy, the coordination mode of the ligand in sulfito complexes of Hg(II) should be considered. In those complexes the S-coordination is clearly superior compared to the O-coordination [37]. Thus, the soft–soft interaction in $HgClO_2^+$ may be the source of the extra stability of the complex. These considerations are in line with structural data for the $(NH_3)_5Co(ClO_2)^{2+}$ complex which confirm O-coordination of the ligand to the hard Co(III) center [31].

4. The redox chemistry of chlorine(III) with metal ions

4.1. Chlorine(III) as a reducing agent

As discussed before, the chlorite ion can be oxidized to higher oxidation state chlorine species with a sufficiently strong oxidant. In the few available kinetic studies, the oxidants were BrO_3^- [38], Br_2 [39,40], HOCl [41–47], SO_4F^- [48], cerium(IV), chromium(VI) and cobalt(III) [30]. Apart from the reactions with the non-metallic species, a detailed kinetic study was reported only for the oxidation by Co(III) [30]. The primary product of this reaction is ClO_2 which is oxidized to ClO_3^- in a subsequent slow reaction step when cobalt(III) is used in excess:

$$HClO_2 + Co^{3+} = ClO_2 + Co^{2+} + H^+ \tag{13}$$

$$ClO_2 + Co^{3+} + H_2O = ClO_3^- + Co^{2+} + 2H^+ \tag{14}$$

No evidence for the buildup of an intermediate chlorito complex was observed in reaction (13).

The coordinated chlorite ion in the $(NH_3)_5Co(ClO_2)^{2+}$ complex also reduces cobalt(III), but considerably slower than free chlorine(III) [30]. The stoichiometry of the reaction was given as follows:

$$\begin{aligned}&(NH_3)_5Co(ClO_2)^{2+} + 2Co^{3+} + 2H_2O\\&= (NH_3)_5Co(H_2O)^{3+} + ClO_3^- + 2Co^{2+} + 2H^+\end{aligned} \tag{15}$$

In this case, the reaction needs to proceed through oxidation state +4 for chlorine, but experimental evidence was not found for transient formation of ClO_2. Interestingly, the very same rate equation was confirmed for all the three oxidation reactions with Co(III) [30,49]:

$$-\frac{d[R]}{dt} = k\frac{[R][Co(III)]}{[H^+]} \tag{16}$$

where R is the chlorine(III) containing reductant, i.e. $HClO_2$, ClO_2 or $(NH_3)_5Co(ClO_2)^{2+}$.

The inverse dependence of the reaction rate on $[H^+]$ was interpreted by assuming that the hydrolysis of cobalt(III) is a rapid preequilibrium and the actual oxidant is the mono-hydroxo complex, $Co(H_2O)_5OH^{2+}$. The corresponding kinetic parameters are listed in Table 2. The difference in the rate constants for reactions (14) and (15) explains why the accumulation of chlorine dioxide was not observed in the oxidation of the chlorito complex. In this system, ClO_2 is generated in a relatively slow step and consumed in a much faster process. On the basis of the kinetic data, the maximum chlorine dioxide concentration was estimated to be 8% of that of the chlorito complex in a typical kinetic run. This corresponded to an absorbance

Table 2
Kinetic data [a] for the oxidation of oxychlorine species by Co(III) [30,49]

Reductant	k [b] (s^{-1})	$\Delta H^{\ddagger}$ ($kJ\ mol^{-1}$)	$\Delta S^{\ddagger}$ ($J\ mol^{-1}\ K^{-1}$)	T (°C)
$HClO_2$	2.6×10^3	64.9	37.7	25.5
ClO_2	103	92.9	104.3	25.5
$(NH_3)_5Co(ClO_2)^{2+}$	4.0	117.6	167.5	20.0

[a] In 2.1 M $LiClO_4$.

[b] On the basis of Eq. (16).

change of about 4% which was insufficient to detect with the experimental technique applied [30].

The reaction between $(NH_3)_5Co(ClO_2)^{2+}$ and fluoroxysulfate ion is also considerably slower than the oxidation of chlorous acid [48]. The amount of ClO_2 formed in this reaction is about 70–80% of that which would be expected if the stoichiometry was 1:1. It is very likely that part of chlorine(III) is oxidized to chlorate ion in a competing reaction step. Quantitative kinetic studies were not reported on this system. It should be noted that the complexity of the reaction is consistent with the results reported for the oxidation reactions of free chlorine(III) by the non-metallic oxidants listed above.

The reduction of the tris(1,10-phenanthroline)iron(III) complex, $Fe(phen)_3^{3+}$, by chlorine(III) is too fast to be monitored directly even by the stopped-flow method [50].

$$Fe(phen)_3^{3+} + ClO_2^- \rightleftharpoons Fe(phen)_3^{2+} + ClO_2 \tag{17}$$

$$K_{16} = \frac{[Fe(phen)_3^{2+}][ClO_2]}{[Fe(phen)_3^{3+}][ClO_2^-]}$$

The equilibrium constant, $K_{17} = 505$, was determined spectrophotometrically by adding sufficient excess of chlorine dioxide to $Fe(phen)_3^{2+}$ and acidifying the samples. Conversion of ClO_2^- into $HClO_2$ shifts the reaction to the left (cf. Eq. (2)) and produces measurable change in $[Fe(phen)_3^{2+}]$. Kinetic studies under the same conditions yielded 2.3×10^7 and 4.5×10^4 $M^{-1}\,s^{-1}$ for the forward and reverse rate constants, respectively. On the basis of the kinetic data, $k_{ex} = 78$ $M^{-1}\,s^{-1}$ was reported for the self-exchange of the ClO_2/ClO_2^- redox couple [50]. Recently, this value was corrected to 3.3×10^4 $M^{-1}\,s^{-1}$ [51] which seems to be more appropriate for the interpretation of outer sphere electron transfer reactions of the ClO_2/ClO_2^- couple [52].

4.2. Chlorine(III) as an oxidant

Chlorine(III) may act either as a one- or a two-electron oxidant and the corresponding reactions may proceed via both inner- and outer-sphere mechanisms. In earlier studies, considerable effort was made to distinguish between the alternative paths and to elucidate the actual course of the reaction. However, a uniform mechanism does not seem to be applicable for these systems and each oxidation reaction needs to be evaluated on a case-by-case basis. The literature data for these reactions are summarized in Table 3.

The oxidation of chromium(II) by chlorine(III) is a relatively fast process characterized with a simple second-order rate law [53]. The lack of hydrogen ion dependence of the rate in 0.1–0.5 M $HClO_4$ is a strong indication that the reactive species is chlorous acid. In strongly acidic solution $[HClO_2]$ is constant and the concentration of ClO_2^- is proportional to the total concentration of chlorine(III) and inversely proportional to $[H^+]$. Thus, the rate should show the corresponding pH dependence if the unprotonated form were reactive.

Table 3
Kinetic data for the oxidation reactions with chlorine(III)

Reductant [a]	Rate law	Parameters [b]	Conditions	Remarks	Ref.
Cr(II)	$\frac{\mathrm{d}[\mathrm{Cr(III)}]}{\mathrm{d}t} = k[\mathrm{Cr(II)}][\mathrm{Cl(III)}]$	$k = 8.1\times10^{4}\ \mathrm{M^{-1}\ s^{-1}}$	0.1–0.5 M $HClO_4$, 5.0°C	No hydrogen ion dependence	[53]
U(IV)	$-\frac{\mathrm{d}[\mathrm{U(IV)}]}{\mathrm{d}t} = k\frac{[\mathrm{U(IV)}][\mathrm{Cl(III)}]}{1+K[\mathrm{HClO_2}])(1+K_\mathrm{p}[\mathrm{H^+}])}$	$k = 291\ \mathrm{M^{-1}\ s^{-1}}$, $\Delta H^{\ddagger} = 106.8$, $\Delta S^{\ddagger} = 159.5$, $K = 4.1\ \mathrm{M^{-1}}$, $K_\mathrm{p} = 21\ \mathrm{M^{-1}}$	2.0 M $NaClO_4$, 25.0°C	In the presence of added phenol	[23]
V(III)	$-\frac{\mathrm{d}[\mathrm{V(III)}]}{\mathrm{d}t} = k[\mathrm{V(III)}][\mathrm{Cl(III)}]$	$k = 75\ \mathrm{M^{-1}\ s^{-1}}$	2.0 M $NaClO_4$, at $[H^+] = 1.0$ M, 25.0°C	Inverse $[H^+]$ dependence	[57]
VO^{2+}	$-\frac{\mathrm{d}[\mathrm{VO^{2+}}]}{\mathrm{d}t} = \frac{k}{1+K_\mathrm{p}[\mathrm{H^+}]}[\mathrm{VO^{2+}}][\mathrm{Cl(III)}]$	$k = 1.3\times10^{3}\ \mathrm{M^{-1}\ s^{-1}}$, $\Delta H^{\ddagger} = 71.1$, $\Delta S^{\ddagger} = 52.3$, $K_\mathrm{p} = 61.6\ \mathrm{M^{-1}}$	1.0 M $NaClO_4$, 25.0°C	In large excess of Cl(III)	[26]
Fe(II)	$-\frac{\mathrm{d}[\mathrm{Fe(II)}]}{\mathrm{d}t} = \left(k_1 + \frac{k_2}{[\mathrm{H^+}]}\right)[\mathrm{Fe(II)}][\mathrm{Cl(III)}]$	$k_1 = 1.9\times10^{3}\ \mathrm{M^{-1}\ s^{-1}}$, $k_2 = 58\ \mathrm{s^{-1}}$	2.0 M $NaClO_4$, 25.0°C	In the presence of added Cl^- and phenol	[59]
$Mo_2O_4^{2+}$	$-\frac{\mathrm{d}[\mathrm{Mo^{V})_2}]}{\mathrm{d}t} = k\frac{[(\mathrm{Mo^{V}})_2][\mathrm{Cl(III)}]}{[\mathrm{H^+}]}$	$k_1 = 670\ \mathrm{s^{-1}}$	1.0 M $NaClO_4$, 25.0°C	In excess oxidant	[60]
B_{12r}	$-\frac{\mathrm{d}[\mathrm{B_{12r}}]}{\mathrm{d}t} = (k_1 + k_2[\mathrm{H^+}])[\mathrm{B_{12r}}][\mathrm{Cl(III)}]$	$k_1 = 2.1\times10^{4}\ \mathrm{M^{-1}\ s^{-1}}$, $k_2 = 5.6\times10^{7}\ \mathrm{M^{-1}\ s^{-1}}$	0.52 M $LiClO_4$, 25.0°C	Mildly acidic pH	[61]
$Fe(phen)_3^{2+}$	$-\frac{\mathrm{d}[\mathrm{Fe(II)}]}{\mathrm{d}t} = \frac{k_1k_2[\mathrm{Fe(II)}][\mathrm{Cl(III)}]}{k_2[\mathrm{phen}] + k_3[\mathrm{Cl(II)}]}$	$k_1 = 3.6\times10^{-4}\ \mathrm{s^{-1}}$	1.0 M $NaNO_3$, 35.0°C	The dissociation of the complex is rate determining	[62]

Table 3 (*Continued*)

Reductant [a]	Rate law	Parameters [b]	Conditions	Remarks	Ref.
$Fe(CN)_6^{4-}$	$-\frac{d[Cl(III)]}{dt}=\frac{a[Fe(II)][Cl(III)]}{b+[Fe(III)]}$		1.0 M $NaNO_3$, 25.0°C	a and b vary with the conditions	[65]
$Fe(II)(tar)_n$	$-\frac{d[Fe(II)]}{dt}=k[Fe(II)][Cl(III)]$	$k=6.2\times10^4$ M^{-1} s^{-1}	1:1 NH_3/NH_4Cl, 27.0°C		[66]
$Fe(II)(cit)_n$	$-\frac{d[Fe(II)]}{dt}=k[Fe(II)][Cl(III)]$	$k=6.3\times10^4$ M^{-1} s^{-1}	1:1 NH_3/NH_4Cl, 27.0°C		[66]
$Fe(edta)^{2-}$	$-\frac{d[Fe(II)]}{dt}=k[Fe(II)][Cl(III)]$	$k=3.0\times10^4$ M^{-1} s^{-1}	1:1 NH_3/NH_4Cl, 27.0°C		[66]
$Cr(NH_3)_5$-OH^+	$-\frac{d[Cr(II)]}{dt}=k[Cr(II)[Cl(III)]$	$k=1.6\times10^4$ M^{-1} s^{-1}	1:1 NH_3/NH_4Cl, 27.0°C		[67]
$Cr(edta)^{2-}$	$-\frac{d[Cr(II)]}{dt}=k[Cr(II)][Cl(III)]$	$k=1.8\times10^3$ M^{-1} s^{-1}	1:1 NH_3/NH_4Cl, 27.0°C		[67]
$V(II)(NH_3)_n$ $-(OH)_y$	$-\frac{d[V(II)]}{dt}=k[V(II)][Cl(III)]$	$k=2.2\times10^5$ M^{-1} s^{-1}	1:1 NH_3/NH_4Cl, 27.0°C		[67]
$V(edta)^{2-}$	$-\frac{d[V(II)]}{dt}=k[V(II)][Cl(III)]$	$k=9.4\times10^4$ M^{-1} s^{-1}	1:1 NH_3/NH_4Cl, 27.0°C		[67]
$Cu(NH_3)_2^+$	$-\frac{d[Cu(I)]}{dt}=k[Cu(I)][Cl(III)]$	$k=44$ M^{-1} s^{-1}	1:1 NH_3/NH_4Cl, 27.0°C		[66]

[a] Phen: 1,10-phenanthroline, tar: tartarate, cit: citrate, edta: ethylenediaminetetraacetate.

[b] $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are given in units of kJ mol^{-1} and J mol^{-1} K^{-1}, respectively.

No evidence was found for the formation of higher oxidation state chlorine species and the observations were consistent with a 4:1 stoichiometry for Cr(II) and Cl(III) up to 95% conversion [53]. The results imply that any intermediate which may form in this system is a sufficiently fast oxidant of chromium(II) and side reactions do not interfere with the oxidation of Cr^{2+}. The analysis of the kinetically inert Cr(III) products showed significant chlorine transfer from the oxidizing agent to chromium(II). This was taken as evidence for an inner-sphere mechanism.

In the chlorine(III)–uranium(IV) reaction, the ratio of the consumed reactants varied from 1.5 to 2.5 depending on the actual pH, the concentrations and concentration ratios of the reactants [54]. On the basis of plausible considerations, Cl(III) should be reduced to Cl^- and U(IV) should be oxidized to U(VI), respectively. The completely different stoichiometry observed experimentally is consistent with the formation of higher oxidation state chlorine species. At first, the oxidation of the oxidizing agent in a highly reducing environment may appear to be contradictory. Nevertheless, a coherent interpretation of the results can be given on the basis of a general mechanism which postulates the formation of a reactive transient species in the initial electron transfer step between the reactants. Subsequently, the intermediate may either oxidize U(IV) and/or generate additional transient species with chlorine(III). The reaction(s) of the intermediate(s) can be in competition with the corresponding reactions of U(IV). In accordance with these considerations, first the following simple model was proposed for the ClO_2^-–U(IV) reaction:

$$\mathrm{U(IV)} + \mathrm{Cl(III)} = \mathrm{U(VI)} + \mathrm{Cl(I)} \tag{18}$$

$$\mathrm{Cl(I)} + \mathrm{Cl(III)} = \mathrm{Cl(V)} + \mathrm{Cl}^- \tag{19}$$

Because the oxidation of U(IV) by Cl(V) is slow and the U(IV)–Cl(I) reaction is much slower than the U(IV)–Cl(III) reaction, half of Cl(III) which is initially present would be consumed by reaction (18), and a 2:1 stoichiometry should prevail for Cl(III) and U(IV) in the limiting case. (The chlorine(I) species was HOCl under the acidic conditions applied.) This ratio of the reactants was exceeded and the formation of chlorine dioxide was observed under certain conditions. Thus, reactions (18) and (19) do not provide an exact description of the system and further reaction paths need to be considered. The relatively slow acid catalyzed decomposition of chlorite ion cannot be the source of ClO_2, and it is reasonable to assume that this species is also formed in the $HClO_2$–HOCl reaction.

As it will be demonstrated in a few other cases in the rest of the paper, the chlorine(III)–hypochlorous acid reaction always plays a very important role in redox processes of chlorite ion when other reaction channels are not available for rapid removal of HOCl formed from chlorine(III). When, as in the oxidation of Cr(II) by Cl(III), HOCl is able to react quickly with the reducing agent [53], no complications arise and the chlorine species are reduced to Cl^-. The rate-determining step is the reduction of chlorite ion and a simple second-order rate law is valid until the completion of the reaction. In contrast, when the reduction of HOCl by the reductant is slow, the kinetic effects of the chlorite ion–hypochlorous acid reaction become more pronounced as HOCl accumulates over the course of the reaction. The following order was established for the relative rates of the reactions of various chlorine species with uranium(IV): $ClO_2^- > ClO_2 > OCl^- > Cl_2 > ClO_3^-$ [54]. This trend is consistent with experimental observations that side reactions interfere with the reduction of chlorine(III) by uranium(IV).

In order to understand the complexity of the oxidation reactions of chlorite ion, a brief survey of the chlorite ion–hypochlorous acid reaction cannot be circumvented. The first detailed study on this system was reported by Taube and Dodgen as early as 1949 [41]. These authors proposed the formation of the Cl_2O_2 intermediate which generates chlorine dioxide and chlorate ion in further reaction steps with another Cl_2O_2 molecule and water, respectively. Subsequent studies on the ClO_2^-–HOCl reaction basically confirmed this mechanism [42–47]. It is generally agreed that lower pH, chlorite ion excess, and higher reactant concentrations make the formation of chlorine dioxide preferable over chlorate ion. The kinetics of the reaction, which becomes very fast with decreasing pH, was not studied under acidic conditions. However, it is very likely that the basic features are retained at low pH, i.e. the overall course of the reaction is expected to be very sensitive to the conditions applied. Therefore, it is not surprising that complex kinetics ensues when the reduction of ClO_2^- by a substrate and its oxidation by hypochlorous acid are kinetically coupled.

In the uranium(IV)–chlorine(III) reaction, the significance of HOCl was confirmed by adding scavengers of hypochlorous acid to the reaction mixture [54,55]. At least in part, hypochlorous acid is converted into Cl_2 and BrCl in the presence of added Cl^-, Br^-, respectively. These species react considerably slower with chlorite ion than HOCl and, because reaction (18) becomes superior over reaction (19), the $[ClO_2^-]/[U(IV)]_{consumed}$ ratio decreases. The addition of phenol completely eliminates reaction (19) and the stoichiometry becomes 1:1. The reaction of HOCl with phenol is relatively slow and cannot account for the observed effect. It was assumed that phenol reacts rapidly with either Cl_2 or Cl_2O_2 which are secondary intermediates in this system [55]. The formation of Cl_2O_2 requires the involvement of a second molecule of chlorous acid:

$$HOCl + HClO_2 = Cl_2O_2 + H_2O \tag{20}$$

Therefore, in order to explain the 1:1 stoichiometry, it must be assumed that one mole of chlorite ion is regenerated in the reaction between phenol and Cl_2O_2.

In the presence of added phenol, the kinetics of the reaction could be studied conveniently [23]. It was shown that the reactive form of chlorine(III) is ClO_2^- and the excess of Cl(III) inhibits the reaction via the formation of an adduct with U(IV). Oxygen-18 tracer experiments indicated significant oxygen transfer from the oxidant to U(IV) and the reaction was described as a two-electron transfer process with direct oxygen bonding in the first coordination sphere of the metal ion.

The reactions of low oxidation state vanadium species with oxychlorine species were extensively studied by Gordon and co-workers. In the vanadium(II)–chlorate ion reaction a straightforward 6:1 stoichiometry was observed implying that chlorous acid and other intermediates react much faster with the metal ion than

ClO_3^- [56]. The same conclusion is supported by kinetic studies on the oxidation of vanadium(III) by the chlorite ion [57]. In this case, the stoichiometry approaches 1:4 for Cl(III) and V(III) in the excess of the metal ion. The reaction was monitored by following the formation of V(IV) at 760 nm. The kinetic traces showed a typical bi-phase kinetic feature. After a fast initial phase, a considerably slower but larger absorbance increase was observed. The slower kinetic process was completely removed by adding phenol to the reaction mixture. Furthermore, the stoichiometry was also altered and 1 mol Cl(III) oxidized only approximately 1 mol vanadium(III). This stoichiometry was taken as evidence that a kinetically significant intermediate, perhaps chlorine(II), is scavenged by phenol. The evaluation of full kinetic traces in the presence and initial rate studies in the absence of phenol confirmed a simple second-order rate equation for the reaction. It was demonstrated that the rate increases by increasing the pH, but the exact pH dependence of the rate law was not reported for this reaction.

Preliminary kinetic studies classified the V(IV)–chlorite ion reaction to be fast and complicated [58]. Our recent studies confirmed that chlorine dioxide formation and the oxidation of the metal ion occur simultaneously in this system [26]. In large excess of chlorine(III), simple first-order kinetic traces were observed at the characteristic d–d band of VO^{2+}. When the excess of chlorite ion was reduced, the initial rapid decrease in the absorbance was followed by a much slower process. The pH dependence of the reaction rate under first-order conditions confirmed that the reactive form of chlorine(III) is chlorite ion. These observations indicate very strong analogy with the V(III)–Cl(III) reaction. Vanadium(IV) is a typical one-electron reducing agent and coherent interpretation of the results implies the formation of a Cl(II) intermediate.

The formation of a transient Cl(II) species also seems to be inevitable in the iron(II)–chlorine(III) reaction [59]. In this case, the $[\mathrm{Fe(III)}]_{\mathrm{produced}}/[\mathrm{Cl(III)}]_{\mathrm{consumed}}$ ratio approaches 4.0 with increasing iron(II) concentration. When chloride ion and phenol are added to the reaction mixture the stoichiometric ratio reduces to 2:1. The combined effect of these two reactants is the same as in the reactions discussed before.

In principle, iron(II) can be oxidized either in a one- or a two-electron-transfer process. The latter path would be consistent with the production of the $Fe_2(OH)_2^{4+}$ dimer in substantial concentration. However, the formation of only a limited amount of the iron(III) dimer was observed and it was attributed to the oxidation of iron(II) by HOCl which is a side reaction in the absence of scavengers. It was concluded that the reduction of chlorine(III) occurs in two consecutive one-electron-transfer steps with the first being rate determining.

$$\mathrm{Fe(II)} + \mathrm{Cl(III)} = \mathrm{Fe(III)} + \mathrm{Cl(II)} \tag{21}$$

$$\mathrm{Fe(II)} + \mathrm{Cl(II)} = \mathrm{Fe(III)} + \mathrm{Cl(I)} \tag{22}$$

An attempt was made to obtain firm evidence for a two-electron-transfer reaction of chlorine(III) in the oxidation of the dimeric $Mo_2O_4^{2+}$ [60]. It was shown that this reductant can easily be oxidized by a series of oxyhalogen species. When the dimer was used in excess, the stoichiometry was always consistent with the transfer of the maximum number of electrons required to yield the corresponding halide ion. The rate of oxidation was found to be inversely proportional to $[H^+]$ confirming that ClO_2^- is the reactive form of chlorine(III). Apparently, the chlorite ion is one of the most efficient oxidant of the molybdenum(V) dimer because the following order was established for the reactivities: $ClO_2^- \gg BrO_3^- > IO_3^- > ClO_3^-$.

The same trend of reactivity was reported for the oxidation of the reduced form of vitamin B_{12}, cob(II)alamin (B_{12r}), by oxyhalogen species [61]. Simple first-order decay of B_{12r} was observed under mildly acidic conditions and in the excess of chlorine(III). The pH dependence of the reaction rate confirmed that both the protonated and unprotonated forms of the oxidant are reactive. An inner-sphere one-electron-transfer mechanism was proposed in which first a reactive Cl(II) intermediate is produced in the rate-determining step. It was assumed that the oxidant is bonded via an oxygen atom to the metal center. This assumption is in line with the considerations regarding the structures of labile chlorito complexes (cf. Section 3.2).

Chlorine(III) is able not only to reduce the $Fe(phen)_3^{3+}$ complex but also to oxidize $Fe(phen)_3^{2+}$ to the corresponding iron(III) complex [62], i.e. the same reactant acts either as a reductant and an oxidant toward the same redox couple. This odd feature of chlorine(III) can be understood by considering the redox potentials of the reactants and the kinetics of the corresponding reactions. The redox potentials for the $Fe(phen)_3^{3+}/Fe(phen)_3^{2+}$ ($\varepsilon^0 = 1.13$ V) [63] and ClO_2/ClO_2^- ($\varepsilon^0 = 0.936$ V) [64] redox couples predict that chlorine dioxide should be stabilized over chlorine(III) as indicated by Eq. (17). Because of the protolytic equilibrium between ClO_2^- and $HClO_2$, the Cl(IV)/Cl(III) potential increases by increasing the acidity and reaction (17) is shifted to the left. However, this change in the equilibrium constant is not the main reason for the oxidation of $Fe(phen)_3^{2+}$. The primary driving force of the reaction is the large oxidation potential of the $HClO_2/HOCl$ couple ($\varepsilon^0 = 1.674$ V) [17] which makes the formation of HOCl favorable. Because the reduction of $Fe(phen)_3^{3+}$ by chlorine(III) [50] is orders of magnitude faster than the oxidation of $Fe(phen)_3^{2+}$ by the same reactant [62], reaction (17) may reach a quasi-equilibrium before the system reaches the thermodynamically stable stage.

The major product of the $Fe(phen)_3^{2+}$–ClO_2^- reaction was identified as the $[(phen)_2Fe(OH)_2Fe(phen)_2]^{4+}$ dimer [62]. It was proposed that the rate-determining step of the reaction is the dissociation of the $[Fe(phen)_3^{2+}]$ complex and the following mechanism accounts for the observations:

$$[Fe(phen)_3^{2+} \rightleftharpoons [Fe(phen)_2]^{2+} + phen \quad k_{23}, k_{-23} \tag{23}$$

$$[Fe(phen)_2]^{2+} + ClO_2^- \rightarrow products \quad k_{24} \tag{24}$$

Standard derivation yields the following rate equation:

$$-\frac{d[Fe(phen)_3^{2+}]}{dt} = \frac{k_{23}k_{24}[Fe(phen)_3^{2+}][ClO_2^-]}{k_{-23}[phen] + k_{24}[ClO_2^-]} \tag{25}$$

In the excess of the oxidant and at low phenanthroline concentration Eq. (25) reduces to a simple first-order rate equation and the experimentally determined rate constant approaches k_{23}. The kinetic results did not allow for unambiguous evaluation of the intimate nature of the electron transfer step.

Under slightly acidic conditions 1 mol chlorite ion oxidizes 4 mol $[Fe(CN)_6]^{4-}$, indicating that side reactions between chlorine(III) and intermediate chlorine species are of marginal kinetic importance. In contrast to the straightforward stoichiometry, a rather complex rate equation was confirmed for this reaction [65]. It was shown that the rate is affected by the pH, the concentration of the phosphate buffer applied and the material of the surface of the reactor. The results were interpreted by assuming that a reversible electron transfer occurs both in the homogeneous solution and at the surface of the reactor. Basically the authors described an interfacial catalysis in which the adsorption of the negatively charged $[Fe(CN)_6]^{4-}$ complex precedes the electron transfer process. The interfacial reaction is suppressed at sufficiently high buffer concentration because the adsorption of the major buffer components, such as HPO_4^{2-}, $H_2P_2O_7^{2-}$ or $HP_2O_7^{3-}$, reduces the surface concentration of the reactants.

A series of oxidation reactions between the chlorite ion and metal complexes was studied by polarography in 1:1 NH_4Cl/NH_3 (1 M each) buffer [66,67]. In these experiments higher oxidation state metal complexes were reduced on a dropping mercury electrode. The re-oxidation of the reduced forms in the presence of chlorite ion produced a catalytic current. The rate constants for the corresponding homogeneous reactions were determined by analyzing the current–potential curves. According to the data, each high-spin, substitution labile complex was rapidly oxidized. No catalytic polarographic current was observed with the substitution inert $Fe(CN)_6^{4-}$ complex which is involved in a relatively slow redox reaction with the chlorite ion. In contrast, the oxidation of the inert V(II)–edta complex was also fast. First, the observations were interpreted by assuming that the oxidant enters the coordination sphere of the complex and the oxidation occurs in an inter-sphere process. Later this model was modified by proposing either an outer-sphere oxygen atom transfer or O^- ion transfer. The details of such a mechanism were not specified and it is not clear how an oxygen atom (with or without charge) could be transferred in an outer-sphere process.

4.3. Catalytic decomposition of chlorine(III)

The formation of higher oxidation state chlorine species was often observed in oxidation reactions with chlorite ion. Typically, the generation of ClO_2 and ClO_3^- was found to be much faster than acid catalyzed decomposition of chlorous acid under similar conditions. This leads to the conclusion that chlorine(III) decomposes in a catalytic process which is controlled by the electron transfer reaction. When the total amount of the substrate is consumed the rate of decomposition relaxes to that of the acid catalyzed path. Catalysis in the classical sense, i.e. when the catalyst retains its oxidation state during the reaction, was reported only in a few cases.

Earlier studies indicated that iron(III) is an efficient catalyst of chlorite ion decomposition [68–70]. On the basis of spectrophotometric experiments a complex rate law was reported for the catalytic decomposition by Schmitz and Rooze [70]. According to those authors, the reaction rate is first order in Fe(III), ClO_2^- and $HClO_2$, inversely proportional to $[ClO_2]$ and exhibits a complex pH dependence. Subsequent studies by Fábián and Gordon were in qualitative agreement with these observations [35]. Time resolved spectrophotometric and single wavelength stopped-flow measurements indicated strong auto-inhibition in this reaction. Quantitative evaluation of the absorbances was obstructed by the large number of absorbing species. Because the spectra of ClO_2^-, $HClO_2$, ClO_2, $Fe(OH)^{2+}$, $Fe_2(OH)_2^{4+}$, $FeClO_2^{2+}$ and possible other iron(III) species strongly overlap, the concentration profiles for the individual components could not be calculated. Advanced fitting procedures gave somewhat ambiguous estimates even for the concentration of chlorine dioxide, which is the dominant absorbing species in this system.

The noted problems were overcome by using the quenched stopped-flow method [35]. In these experiments, the injection of NaF solution into the reaction mixture immediately stopped the decomposition because the total amount of iron(III) was rapidly converted into catalytically inactive and colorless fluoro complexes. Thus, the quenched samples could conveniently be analyzed for various oxidation state chlorine species by potentiometric and spectrophotometric methods. Kinetic data from the sub-second to several hours time domain confirmed that the concentration ratios of the reacted chlorite ion and the products changed over the course of the reaction. Depending on the actual conditions, the final stoichiometry could be given as the appropriate combination of reactions (2) and (3). Several kinetic runs made in the closed quenched stopped-flow apparatus were repeated in an open reactor by continuously purging the reaction mixture with nitrogen. The conversion of chlorine(III) at the same reaction time substantially increased by the removal of ClO_2 confirming that the auto-inhibition is due to this species. A very similar auto-inhibition of ClO_2 was found recently in the Br_2–ClO_2^- reaction [40].

On the basis of combined stopped-flow, quenched stopped-flow and conventional batch experiments, a detailed kinetic model was postulated for the iron(III) catalyzed decomposition of chlorine(III) (Table 4) [35]. According to this model, the catalytic cycle is initiated by rapid formation of the $FeClO_2^+$ complex (cf. Section 3.2). The chlorito complex decomposes into iron(II) and ClO_2 in a reversible rate-determining step. This reaction is not favored thermodynamically, but subsequent steps carry the decomposition to completion. As the reaction proceeds, ClO_2 is formed in increasing concentration and retards the overall rate by shifting the decomposition of the complex backward. The oxidation of iron(II) by chlorine(III) and subsequent reactions of the intermediate chlorine species are presumably fast. Although these reactions occur after the rate-determining step, their relative rates are of crucial importance because the final stoichiometry of the reaction is determined by the delicate balance between the competing reaction paths leading to the formation of ClO_2 and ClO_3^-. The mechanism was validated by model calculations. The agreement between measured and calculated kinetic traces is demonstrated in Fig. 4.

Table 4
Kinetic model for the iron(III) catalyzed decomposition of chlorine(III) [25,35]

Reaction	Rate constant	
$H^+ + ClO_2^- = HClO_2 \quad K_p = 52.5\ M^{-1}$		Fast equilibrium
$Fe^{3+} = Fe(OH)^{2+} + H^+ \quad K_h = 1.82 \times 10^{-3}\ M$		Fast equilibrium
$Fe^{3+} + ClO_2^- = FeClO_2^{2+}$	k_{Fe3}	$4.4 \times 10^2\ M^{-1}\ s^{-1}$
$K_{Fe} = 13.8\ M^{-1}$	k_{-Fe3}	$31.6\ s^{-1}$
$FeClO_2^{2+} = Fe^{2+} + ClO_2$	k_{Fe4}	$100\ s^{-1}$
$K_4 = 2.0 \times 10^{-5}\ M$	k_{-Fe4}	$7.6 \times 10^6\ M^{-1}\ s^{-1}$
$Fe^{2+} + ClO_2^- \rightarrow Fe^{3+} + Cl(II)$	k_{Fe5}	$1.9 \times 10^3\ M^{-1}\ s^{-1}$
$Fe^{2+} + HClO_2 \rightarrow Fe^{3+} + Cl(II)$	k_{Fe6}	$3.0 \times 10^3\ M^{-1}\ s^{-1}$
$ClO_2^- + Cl(II) \rightarrow HOCl + ClO_2$	k_{Fe7}	Very fast
$HOCl + HClO_2 = Cl_2O_2 + H_2O$	k_{Fe8}	$2.1 \times 10^4\ M^{-1}\ s^{-1}$
$Cl_2O_2 + ClO_2^- = 2ClO_2 + Cl^-$	k_{Fe9}	$5.0 \times 10^8\ M^{-1}\ s^{-1}$
$Cl_2O_2(+H_2O) = ClO_3^- + Cl^- + 2H^+$	k_{Fe10}	$1.0 \times 10^7\ s^{-1}$
$HOCl + Cl^- + H^+ = Cl_2\ (+H_2O)$	k_{Fe11}	$1.8 \times 10^4\ M^{-2}\ s^{-1}$
$K_{12} = 1.7 \times 10^3\ M^{-2}$	k_{-Fe11}	$1.1 \times 10^1\ s^{-1}$
$Cl_2 + ClO_2^- = Cl_2O_2 + Cl^-$	k_{Fe12}	$3.7 \times 10^3\ M^{-1}\ s^{-1}$

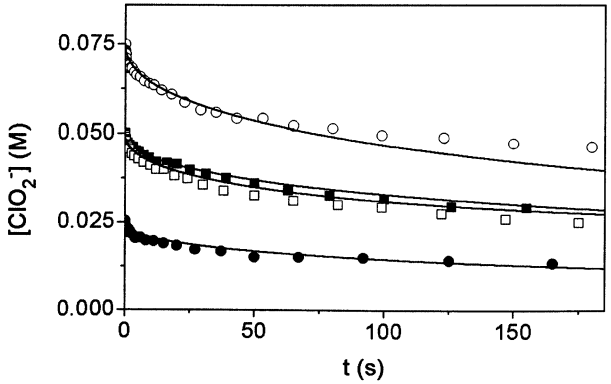


Fig. 4. Experimental and calculated (solid lines) concentration profiles for iron(III) catalyzed decomposition of chlorine(III). $[Fe(III)] = 1.4 \times 10^{-3}$ M, $[Cl(III)]_0 = 7.5 \times 10^{-2}$ M, pH 1.75 (○); $[Fe(III)] = 1.4 \times 10^{-3}$ M, $[Cl(III)]_0 = 5.0 \times 10^{-2}$ M, pH 1.25 (■); $[Fe(III)] = 1.4 \times 10^{-3}$ M, $[Cl(III)]_0 = 5.0 \times 10^{-2}$ M, pH 2.00 (□); $[Fe(III)] = 1.4 \times 10^{-3}$ M, $[Cl(III)]_0 = 2.5 \times 10^{-2}$ M, pH 1.75 (●); 1.0 M $NaClO_4$, 25.0°C [35].

The decay and in certain cases the disappearance of the characteristic yellow color of ClO_2 indicated unique kinetic phenomena in acidic aqueous solution of chlorine(III), chlorine dioxide and mercury(II) [71]. A simple explanation for the observations is not readily available on the basis of the general chemical properties of these species. In an oxidative environment, $+2$ is the stable oxidation state of mercury, chlorine dioxide is stable under acidic condition and no reaction was observed between these species in the absence of chlorine(III). Direct reaction between chlorine dioxide and chlorine(III) is not known either and the decomposi-

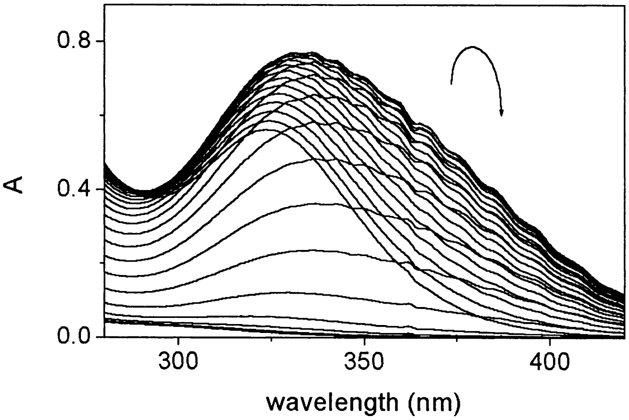


Fig. 5. Time resolved spectra in the mercury(II)–chlorine(III) reaction: [Hg(II)] = 0.030 M, $[Cl(III)]_0$ = 0.012 M, $[H^+]$ = 0.350 M, t = 0–25 s, 1.0 M $NaClO_4$, 25.0°C.

tion of chlorine(III) leads to the formation of ClO_2 as a final product in acidic solution. These considerations imply that the decay of chlorine dioxide occurs via a complex redox process in which the chlorito complex of mercury(II) plays an important role [33].

Time resolved spectra for the mercury(II)–chlorite ion reaction are shown in Fig. 5. The fine structure of the spectra is characteristic of chlorine dioxide which is formed much faster in the presence than in the absence of mercury(II). After reaching a maximum, $[ClO_2]$ decreases to 0 at about 25 s. Because the formation of the $HgClO_2^+$ complex is diffusion controlled, the concentration ratio of the chlorito complex and free chlorine(III) is constant during the reaction provided that the pH does not change and mercury remains in + 2 oxidation state. Thus, the disappearance of the characteristic absorbance maximum of $HgClO_2^+$ at the end of the reaction confirms that the total amount of chlorine(III) is consumed. Precipitation was not observed upon addition of excess chloride ion to the spent reaction mixture and the formation of Hg(I) could be excluded.

The kinetic profiles showed significant variation as a function of reagent concentration and pH. In excess Hg(II), autocatalytic formation of chlorine dioxide was found. The transient amount of ClO_2 was increased by decreasing the [Hg(II)]/[Cl(III)] concentration ratio and decreasing the acidity. However, the basic feature of this system, i.e. the decay of $[ClO_2]$ at the end of the reaction, was not altered by varying the reactant concentrations within a relatively wide range. It should be added that some ClO_2, produced in the initial phase, remained in the reaction mixture under certain conditions. Essentially the observations can be interpreted in terms of a mercury(II) catalyzed decomposition of chlorine(III). This system is special in that chlorine dioxide is not a final product in the decomposition. The following general mechanism was proposed for the reaction:

$$H^{+} + ClO_2^{-} \rightleftharpoons HClO_2 \quad \text{fast} \tag{2a}$$

$$Hg^{2+} + ClO_2^{-} \rightleftharpoons HgClO_2^{+} \quad \text{fast} \tag{26}$$

$$ClO_2^{-} \rightarrow ClO_2 + ClO_3^{-} + Cl^{-} \quad \text{slow initiation} \tag{27}$$

$$HgClO_2^{+} + ClO_2 \rightarrow Hg^{2+} + ClO_3^{-} + Cl(II) \quad \text{rate determing} \tag{28}$$

$$ClO_2^{-} + Cl(II) + H^{+} \rightarrow ClO_2 + HOCl \quad \text{fast} \tag{29}$$

$$ClO_2 + Cl(II) \rightarrow ClO_3^{-} + HOCl \quad \text{fast} \tag{30}$$

$$ClO_2^{-} + HOCl \rightarrow ClO_2 + Cl^{-}(+ClO_3^{-}) \quad \text{fast} \tag{31}$$

In this model, the speciation of the unreacted chlorine(III) is controlled by the first two reactions which are fast pre-equilibria. The autocatalytic cycle is triggered by chlorine dioxide formed in the slow, acid catalyzed decomposition of chlorine(III) in reaction (27). Reaction (28) is an essential step in the model. It assumes that coordination to the metal center perturbs the electron structure of chlorite ion such that it is able to oxidize chlorine dioxide in a direct reaction by transferring an O^{-} ion. The autocatalytic cycle includes reactions (28)–(31) in which more chlorine dioxide is produced than consumed. Furthermore, the relative rates of these reactions determine how much ClO_2 remains at the end of the overall reaction.

The formation of a Cl(II) intermediate was postulated in quite a few mechanisms for the redox reactions of chlorine(III). Although direct experimental evidence is not available to identify this species, most likely it is ClO which has a very short lifetime in aqueous solution. On the basis of pulse radiolytic experiments [72], ClO seems to be an oxidant strong enough to facilitate one-electron oxidation of ClO_2^{-} and ClO_2 to higher oxidation state chlorine species as suggested by reactions (29) and (30).

5. A final remark

The reactions of chlorine(III) with metal ions exhibit an amazingly rich redox chemistry. In spite of the diversity of these reactions a general pattern appears to emerge from the analysis of the available literature data. As a reductant, chlorine(III) is oxidized to chlorine dioxide and/or chlorate ion in simple one-electron-transfer steps. Metal ion catalyzed disproportionation and oxidation reactions of chlorine(III) often proceeds via the formation of chlorito complexes or adducts between the reactants. The formation of reactive intermediates and their reactions with each other and the reactants form the very basis of the complex kinetic behavior observed in these systems. A consequence of the competition between the kinetically coupled reaction paths is that the stoichiometries of the corresponding reactions are kinetically controlled. Better understanding of the redox chemistry of chlorine(III) relies on direct detection, identification and thorough characterization of the reactive intermediates formed in these systems. Recent technical developments in kinetic methods may provide the appropriate tools to achieve this ambitious goal.

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