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Complex-Formation Kinetics of Iron(III) with Chlorite Ion in Aqueous Solution. Mechanistic Information from Pressure Effects

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The complex formation kinetics between iron(III) and chlorite ion was investigated as a function of pressure at 5 °C and 1.0 M $NaClO_4$ by using a stopped-flow technique. As auxiliary data, the stability constant and molar reaction volumes were determined for the equilibria $H^+ + ClO_2^- \rightleftharpoons HClO_2$ (log $K_p = 1.56 \pm 0.04$, $\Delta\bar{V}_p = +10.7 \pm 1.5$ cm^3 mol^{-1}) and $Fe^{3+} + ClO_2^- \rightleftharpoons FeClO_2^{2+}$ (log $K_1 = 1.12 \pm 0.05$, $\Delta\bar{V}_1 = +16.5 \pm 2.7$ cm^3 mol^{-1}). It was shown that the complex formation predominantly occurs via the conjugate acid/conjugate base pathway according to an I_d mechanism: $Fe(OH)^{2+} + HClO_2 \rightarrow FeClO_2^{2+} + H_2O$, where $k_1' = (3.0 \pm 0.2) \times 10^3$ M^{-1} s^{-1} and $\Delta V_1^{\ddagger} = +6.9 \pm 2.3$ cm^3 mol^{-1}. A comparison of the results with literature data revealed an analogy between the formation mechanisms of complexes $FeClO_2^{2+}$ and FeN_3^{2+}. In contrast, the mechanism of the formation of the $FeNCS^{2+}$ complex was described as I_a before. This mechanistic changeover is interpreted in terms of the nucleophilic strength of the ligands. It is suggested that, in general, the mechanism of complex-formation reactions of iron(III) can be controlled by the nucleophilicity of the donor group on the entering ligand. Mechanistic implications of the results for the iron(III)-catalyzed decomposition of chlorite ion are also discussed.

Introduction

In redox reactions between metal ions and chlorine(III), complex formation with chlorite ion is generally considered to be one of the key reaction steps.[1-3] Nevertheless, only limited information is available for these complexes.[4,5] Recently, two novel chlorito complexes were reported with copper(II) and iron(III) by Fábián and Gordon.[6,7] It was suggested that both $CuClO_2^+$ ($K = 1.04$ M^{-1})[6] and $FeClO_2^{2+}$ ($K = 13.8$ M^{-1})[7] can be regarded as model compounds for chlorito complexes with di- and trivalent metal ions, respectively.

Iron(III) strongly catalyzes the decomposition of chlorite ion.[8-10] The initial phase of the decomposition appears to be controlled by the formation of the $FeClO_2^{2+}$ complex and its subsequent redox decomposition. In our recently proposed mechanism,[10] the catalytic cycle includes the formation of iron(II) which is rapidly oxidized to iron(III) by various chlorine species. However, an alternative redox cycle via iron(IV) could not be indisputably excluded.[7,10] Since both iron(II) and iron(IV) would form at extremely low concentration levels, direct detection of the transient species seemed to be unattainable.

The need for a more accurate mechanistic description of the catalytic decomposition of chlorite ion, as well as for a better characterization of the chlorito complexes, called for further investigation of these systems. Many chemical reactions, and complex-formation reactions in particular, show characteristic pressure dependencies.[11,12] This makes possible to distinguish alternative mechanisms and to assign the dominant pathways even in complex reaction systems. In the present study the formation kinetics of the $FeClO_2^{2+}$ complex has been investigated as a function of pressure. The results provide additional information for the detailed mechanistic description of the iron(III)–chlorite system.

Experimental Section

Chemicals. The purification of $NaClO_2$ from commercially available sodium chlorite (Janssen; unstabilized; approximately 80% purity) and the preparation of the iron(III) stock solutions from $Fe(ClO_4)_3 \cdot xH_2O$ (Aldrich; low chloride; [Cl^-] < 0.005%) were described earlier.[6,7,13] Other chemicals, $NaClO_4 \cdot H_2O$ and $HClO_4$ (Merck), were the highest purity commercially available and used without further purification. In the kinetic experiments, the concentration of ClO_2^- and the pH were varied in the ranges 0.05–0.25 M and 0.67–2.73, respectively. The iron(III) concentration was 1.04×10^{-3} M. The ionic strength was adjusted to 1.0 M with sodium perchlorate.

Methods. The experiments were performed on a high-pressure stopped-flow device at pressures up to 1250 bar.[14] In order to accommodate the kinetics to the dead-time of the instrument, the measurements were done at 5.0 ± 0.2 °C instead of the previously used 25 °C. After about 20 min of thermal equilibration, each trace was taken as the average of at least five repetitive runs.

In order to avoid interference from the acid-catalyzed decomposition of ClO_2^-, the protonation constant (K_p) of this species was determined by the stopped-flow method. Solutions of $HClO_4$ in up to 1.0 M concentration were mixed with a 0.0204 M $NaClO_2$ solution, and the absorbance jumps were recorded at 305 nm. In these experiments, the observation cell was refilled with the background solution (1.0 M $NaClO_4$) before adjusting each pressure. Thus, the instrument could be calibrated such that the observed output signal was always proportional to the absorbance.

In the kinetic experiments the same calibration method was applied at 250 bar. However, at higher pressures the instrument was not recalibrated. Therefore, because of some baseline drift, only the signals obtained at 250 bar were considered strictly proportional to the absorbance.

Kinetic measurements were carried out by mixing sodium chlorite and acidic iron(III) solutions. In accordance with previous observations, single exponential traces were obtained at 510 nm, which were fitted with a nonlinear least-squares routine.[15] The pseudo-first-order rate constants (k) were reproducible within 5%. The kinetic parameters were obtained

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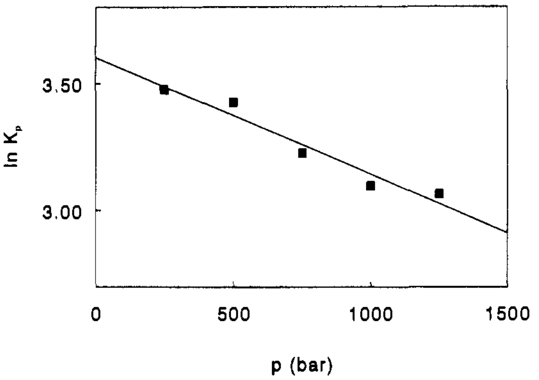

Figure 1. Pressure dependence of the protonation constant of chlorite ion at 5 °C and $I = 1.0$ M.

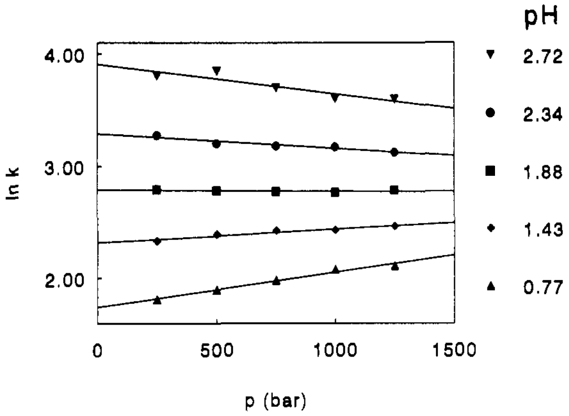

Figure 2. Pressure dependence of the observed pseudo-first-order rate constant for the formation of the $FeClO_2^{2+}$ complex as a function of pH at 5 °C and $I = 1.0$ M. $[ClO_2^-]_T = 0.100$ M; $[Fe^{3+}]_T = 1.04 \times 10^{-3}$ M.

by fitting the appropriate analytical expressions to the experimental data by using the program NESSIE,[15] which minimizes the relative deviations, $\sum[(k_{calc} - k_{exp})/k_{exp}]^2$. The list of concentrations and the measured and calculated rate constants are given as supplementary material.

Results

Equilibria. The protonation constant of chlorite ion was calculated from the acid dependence of the absorbance at each pressure. The appropriate plot of K_p as a function of pressure is shown in Figure 1. The extrapolated protonation constant at ambient pressure (1 bar) and the reaction volume are log K_p = 1.56 ± 0.04 and $\Delta\bar{V}_p = +10.7 \pm 1.5$ cm^3 mol^{-1}, respectively.

It was shown earlier that, on mixing solutions of chlorite ion and iron(III), the stopped-flow traces at 510 nm are consistent with the formation of the $FeClO_2^{2+}$ complex, which is the only absorbing species.[7] Thus, the stability constant of $FeClO_2^{2+}$ at 250 bar was calculated from the concentration dependence of the amplitudes by using the program PSEQUAD.[16] In these calculations $HClO_2$ (log K_p = 1.51) and $Fe(OH)^{2+}$ (log K_h = −3.25) were included with fixed stability constants. The hydrolysis constant of iron(III) was extrapolated from log K_h = −2.74 (25 °C and 1 bar)[17] by using ΔH_h = 40.3 kJ mol^{-1} and $\Delta\bar{V}_h$ = +0.8 cm^3 mol^{-1} given by Swaddle and Merbach.[18] Other hydroxo species were considered to be present at negligible concentration levels. The amplitudes were fitted with an average 8% deviation. The stability constant of the $FeClO_2^{2+}$ complex at 250 bar is log K_1 = 1.04 ± 0.03.

Kinetics. The pressure dependence of the pseudo-first-order rate constants is illustrated in Figure 2. In acidic solutions the reaction is slightly accelerated by increasing pressure, while at higher pH values this trend is reversed. The observations indicate a changeover in the kinetically dominant reaction component on varying the pH.

Under the applied conditions, the following kinetic model was considered:[7]

$$Fe^{3+} + ClO_2^- \rightleftharpoons FeClO_2^{2+} \quad k_1, k_{-1} \tag{1}$$

$$Fe(OH)^{2+} + ClO_2^- \rightleftharpoons Fe(OH)ClO_2^+ \quad k_2, k_{-2} \tag{2}$$

$$Fe(OH)ClO_2^+ + H^+ \rightleftharpoons FeClO_2^{2+} \quad K_3\text{, fast equilibrium} \tag{3}$$

The model implies that the proton-transfer reactions between Fe^{3+}–$Fe(OH)^{2+}$ and $HClO_2$–ClO_2^- are in fast preequilibria. An additional step with the protonated form of the ligand, $Fe^{3+} + HClO_2 \rightleftharpoons FeClO_2^{2+} + H^+$, was expected to be negligible and was rejected from the model.[7,10] Moreover, in the formal kinetic considerations no distinction was made between reaction 1 and the equivalent $FeOH^{2+} + HClO_2$ pathway (see Discussion).

By taking into account that $Fe(OH)ClO_2^+$ is in steady state and $[ClO_2^-]_T \gg [Fe^{3+}]_T$, the following expression can be given for the observed rate constant:

$$k = Q[ClO_2^-]_T\left(k_1 + \frac{k_2K_h}{[H^+]}\right) + k_{-1} + \frac{k_{-2}}{K_3[H^+]} \tag{4}$$

where

$$Q = \frac{[H^+]}{([H^+] + K_h)(1 + K_p[H^+])}$$

and

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

$$K_1 = \frac{[FeClO_2^{2+}]}{[Fe^{3+}][ClO_2^-]} \qquad K_h = \frac{[Fe(OH)^{2+}][H^+]}{[Fe^{3+}]}$$

$$K_3 = \frac{[FeClO_2^{2+}]}{[Fe(OH)ClO_2^+][H^+]}$$

At this point, it should be emphasized that the rate of the iron(III)-catalyzed decomposition of chlorite ion is comparable with that of the complex-formation reaction. Since the decomposition of the chlorito complex proceeds through a reactive transient species,[7,10] the relevant rate constant is incorporated in the dissociation terms of eq 4.

First, the experimental data were fitted on the basis of eq 4. Since chlorite ion was always in large excess over iron(III), the pH was determined by the acid–base equilibria of the ligand and the effect of complex formation and hydrolytic reactions of the metal ion was negligible. Thus, the equilibrium hydrogen ion concentration could be calculated with the usual precision even without knowing the actual stability constant of the chlorito complex at pressures other than 250 bar.

Preevaluation of the data indicated that the complex formation via the $Fe(OH)^{2+}$ complex is of marginal kinetic importance. Accordingly, the observed inverse hydrogen ion concentration dependence of the rate constants needs to be attributed to the redox decomposition of the chlorito complex. Thus, eq 4 can be rewritten in the following linearized form:

$$\frac{k}{Q[ClO_2^-]_T + K_1^{-1}} = k_1 + \frac{k_r}{(Q[ClO_2^-]_T + K_1^{-1})[H^+]} \tag{5}$$

where k_r is the rate constant for the redox decomposition. As illustrated in Figure 3, the experimental data are consistent with this simplified equation.

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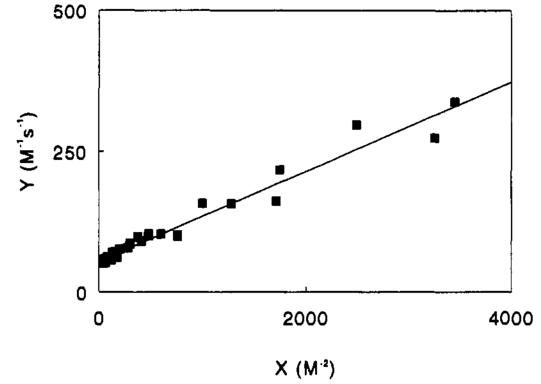

Figure 3. Plot of the experimental data at 250 bar according to eq 5, where, $X = 1/((Q[ClO_2^-]_T + K_1^{-1})[H^+])$ and $Y = k/(Q[ClO_2^-]_T + K_1^{-1})$.

Table I. Thermodynamic and Kinetic Parameters for the Complex Formation of Chlorite Ion with Aqueous Iron(III) at 1 bar, 5 °C, and 1.0 M Ionic Strength

reacn	parameter[a]	
$H^+ + ClO_2^- = HClO_2$	log K_p	1.56 ± 0.04
	$\Delta\bar{V}_p$	+10.7 ± 1.5 cm³/mol⁻¹
$Fe^{3+} + ClO_2^- = FeClO_2^{2+}$	log K_1	1.12 ± 0.05
	$\Delta\bar{V}_1$	+16.5 ± 2.7 cm³/mol⁻¹
	k_1	62.5 ± 4.0 M⁻¹ s⁻¹
	ΔV_1^*	+6.9 ± 2.3 cm³/mol⁻¹
$FeClO_2^{2+} \rightarrow$ products	k_r	(8.5 ± 0.5) × 10⁻² M s⁻¹
	ΔV_r^*	1.5 ± 1.4 cm³ mol⁻¹

[a] Equilibrium and rate constants are extrapolated values; see text.

In agreement with these findings, in the four-parameter fitting procedure using eq 4, the calculated value for k_2 converged to 0 at each pressure. At 250 bar, the calculated k_1/k_{-1} ratio agreed within 10% with K_1 obtained from the amplitudes, and the k_{-2}/K_3 parameter could also be calculated with a 5% standard deviation. According to the results, if the last term in eq 4 corresponds to the dissociation of the chlorito complex via reactions 2 and 3 the complex formation should be much faster via the hydroxo complex than in reaction 1. Therefore, the fitting process should be more sensitive for k_2 than for k_1. As discussed above, it is clearly not the case. This strongly suggests again that the $1/[H^+]$ dependence of the rate constants is characteristic for the redox decomposition of $FeClO_2^{2+}$.

In the final evaluation, all experimental data were fitted simultaneously based on the following expression:

$$k = (Q[ClO_2^-]_T + K_1^{-1}e^{(\Delta\bar{V}_1/RT)\Delta p})k_1e^{-(\Delta V_1^*/RT)\Delta p} + \frac{1}{[H^+]}k_re^{-(\Delta V_r^*/RT)\Delta p} \quad (6)$$

where ΔV_1^* and ΔV_r^* are activation volumes and Δp is the difference between the actual pressure and 250 bar. In these calculations K_1 was included with a fixed value at 250 bar, and parameters k_1 and k_r were obtained for the same pressure. In additional regressions K_1 was also fitted. The parameter values varied within less than one standard deviation compared to the other fitting process. The kinetic data at ambient pressure were extrapolated from the results at 250 bar (Table I).

Due to the small positive value of ΔV_r^*, the decomposition rate of the chlorito complex is slightly affected by the pressure. Therefore, the pressure dependence of k (Figure 2) is determined by the ratio of the forward and reverse rate of reaction 1. From the data in Table I, $\Delta V_{-1}^* = -9.6$ cm³ mol⁻¹. Thus, at low-pH values, where the contribution of the dissociation step to the overall process is relatively high, k increases with the pressure. As the forward reaction becomes more important by increasing the pH, the pressure dependence follows the opposite trend.

To some extent, the results contradict the previously proposed model, which assumes that the redox decomposition of the chlorito complex is pH independent.[7] Thus, the experimental data at 25 °C and 1 bar were reevaluated on the basis of eq 6 ($\Delta p = 0$!) by using a fixed value for K_1. The comparison of the standard deviation, 6.8%, with the earlier reported 6.4% clearly shows that the two models are statistically identical and give equally reliable interpretation of the data. However, on the basis of 6, the calculated value for k_1 at 25 °C is 436 M⁻¹ s⁻¹ instead of the earlier published 269 M⁻¹ s⁻¹.[7]

Discussion

The equilibrium constants obtained in this work compare favorably with those at 25 °C (log K_p = 1.72, log K_1 = 1.14).[6,7] According to earlier studies, the pressure dependence of the protonation constants of weak acids shows a relatively large variation ($\Delta\bar{V}_p$ = +6.0 to +30.0 cm³ mol⁻¹).[11] Since the volume change for taking up a H^+ ion is a constant contribution (*ca.* +4.5 cm³ mol⁻¹), the noted variation is a consequence of specific solvation effects on the anion.[19] Though no correlation was postulated between $\Delta\bar{V}_p$ and the protonation constants, these reactions typically feature positive reaction volumes. The result presented here, $\Delta\bar{V}_p$ = +10.7 ± 1.5 cm³ mol⁻¹, agrees well with these findings.

The equilibrium molar volume change for complex formation reactions of iron(III) is characteristically positive[11] in the order of +10.0 cm³ mol⁻¹. The $\Delta\bar{V}$ value for the $FeClO_2^{2+}$ complex is very consistent with these literature data. In contrast, the activation volume for the same reaction is somewhat unexpected. For ligand substitution reactions of aqueous $Fe(H_2O)_6^{3+}$, negative activation volumes were reported by a variety of ligands (Cl^-, Br^-, NCS^-, H_2O, *etc.*). This is consistent with an associative (I_a) mode of activation.[11] Depending on the charge and nucleophilicity of the entering ligand, certain variation can be anticipated in these activation parameters. However, the value of +6.9 cm³ mol⁻¹ for the reaction of ClO_2^- is clearly out of the acceptable range.

Very recently, a similar atypical activation volume was published for the iron(III)–azide system by Grace and Swaddle.[20] According to these authors, the complex-formation reaction occurs via the conjugate acid/conjugate base (CACB) pathway. On the basis of the rate law, this path is indistinguishable from the $Fe(H_2O)_6^{3+} + N_3^-$ step. Most likely, the same interpretation is also valid for the $Fe(H_2O)_6^{3+} + ClO_2^-$ system and reaction 1 needs to be rewritten in the following form:

$$Fe(OH)^{2+} + HClO_2 = FeClO_2^{2+} + H_2O \quad k_1', k_{-1}' \quad (7)$$

In aqueous solution, the kinetic data for ligand substitution reactions of $Fe(H_2O)_5OH^{2+}$ are consistent with dissociative activation (I_d).[11,18] The activation volumes do not show large variation and scatter around the activation volume for the water exchange on $Fe(H_2O)_5OH^{2+}$, +7.0 cm³ mol⁻¹.[18] The excellent agreement of ΔV_1^* = +6.9 cm³ mol⁻¹ with this value strongly supports the CACB mechanism in the iron(III)–chlorite system. Since the schematic representation of the possible types of ligand substitution mechanisms has been published in recent literature,[11,12] it is not reproduced here. Providing that the above considerations are correct, a value of (3.0 ± 0.2) × 10³ can be estimated for the rate constant k_1' from K_p, K_h, and k_1. This result is also in line with literature data for analogous reactions.[21]

Reaction 7 implies that the complex formation is completed with a fast intramolecular proton-transfer step between the metal ion center and the coordinated ligand. According to an alternative interpretation, the acid–base neutralization may precede the actual ligand substitution step. In this case, the two pathways represented

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Table II. Formation Rate Constants for $Fe^{3+} + L^- = FeL^{2+}$ Reactions

ligand	pK_a	k_1 ($M^{-1}\,s^{-1}$)[a]	I (M)	T (°C)	ref	k_1' ($M^{-1}\,s^{-1}$)[b]
$C_2H_5COO^-$	4.7	4.2×10^5	1.0	20	22	4.6×10^3
CH_3COO^-	4.6	3.4×10^5	1.0	20	22	4.7×10^3
N_3^-	4.2	1.6×10^5	1.0	25	23	5.5×10^3
F^- [c]	2.9	5.4×10^3	0.5	25	24	3.7×10^3
CH_2ClCOO^-	2.6	4.9×10^3	1.0	20	22	6.8×10^3
ClO_2^-	1.7	436[d]	1.0	25	7	4.9×10^3
$H_2PO_2^-$	0.9	270	1.0	25	25	1.9×10^4
SCN^-	0.9	127	0.4	25	26	8.8×10^3

[a] k_1 is defined by assuming $Fe^{3+} + L^- = FeL^{2+}$. [b] k_1' is defined by assuming $FeOH^{2+} + HL = FeL^{2+} + H_2O$; $k_1' = k_1K_a/K_h$. Rate constant k_1 was converted into k_1' by using $K_h = 1.82 \times 10^{-3}$ M.[17] The variation of K_h as the function of temperature and ionic strength is expected to generate less than 10% error in k_1'. [c] The rate constant was estimated on the basis of the corresponding activation parameters obtained from the 0–12.1 °C range. [d] Reevaluated value; see text.

by reactions 1 and 7 would be different only if the proton-transfer step between $Fe(OH)^{2+}$ and $HClO_2$ were rate determining. However, the proton-transfer reactions of simple acid–base pairs are typically close to the diffusion-controlled limit. The estimated rate constants for the protonation of $Fe(OH)^{2+}$ and the acid dissociation of $HClO_2$ are $\sim 10^{10}\ M^{-1}\,s^{-1}$ and $> 10^8\ s^{-1}$ ($10^{10}/K_p$), respectively. According to these data, the proton-transfer reactions are several orders of magnitude faster than the ligand substitution steps and cannot be rate determining. Consequently, the alternative interpretation can be rejected.

In earlier literature, a reasonable correlation was found between the rate constants for the $Fe(H_2O)_6^{3+} + L^-$ reaction and the pK_a of the ligand.[22] It was taken as evidence for an I_a mechanism. As shown in Table II, when converted into k' for the alternative $Fe(H_2O)_5OH^{2+} + HL$ pathway, the same data are also consistent with an I_d mechanism. According to pressure-dependent studies, both mechanisms can be operative in these reactions. As discussed above, the reactions with N_3^- and ClO_2^- proceeds via the I_d CACB pathway, while the activation volume for the reaction with NCS^-, $\Delta V^{\neq} = -5.7\ cm^3\,mol^{-1}$,[20] is consistent with an I_a mechanism.

In the I_a mechanism, bond making between the metal ion and entering ligand dominates the transition state. It implies that the ability of the ligand to penetrate the primary solvation sphere and to attack the metal ion center determines the course of the reaction. The observed mechanistic changeover can be interpreted by taking into account the nucleophilic strength of the ligands. Providing that the nucleophilicity scale based on the reactions of platinum(II)[28] also holds for iron(III), the I_a mechanism seems to be more preferable with NCS^- ($n_{Pt}^0 = 5.65$) than with N_3^- ($n_{Pt}^0 = 3.58$). No nucleophilicity data are available for chlorite ion. However, oxygen donors tend to be poor nucleophiles and the n_{Pt}^0 value for ClO_2^- is expected to be smaller than for N_3^-. It follows that the reaction of $Fe(H_2O)_6^{3+}$ with relatively strong nucleophiles, such as NCS^-, is fast via an associative (I_a) activation. On decreasing of the nucleophilicity, this pathway slows down and eventually the CACB pathway, which is controlled through I_d activation by the fast water exchange on $Fe(H_2O)_5OH^{2+}$, becomes dominant. Consequently, weak nucleophiles react according to an I_d mechanism.

The above considerations strongly suggest that the mechanism of ligand substitution reactions of iron(III) can be tuned by altering the nucleophilicity of the entering ligands. Moreover, on the basis of the limited data discussed here, the basicity of the ligand appears to be less significant with respect to the mechanism than it was suggested before. Further experimental work should address how specific properties of the ligand, *i.e.* basicity, nucleophilicity, hard–soft character of the donor atom(s), *etc.*, may affect the intimate mechanism of these reactions.

The previously proposed mechanism for the iron(III)-catalyzed decomposition of chlorite ion postulates that the catalytic cycle is initiated by the decomposition of the $FeClO_2^{2+}$ complex:[10]

$$FeClO_2^{2+} \rightleftharpoons Fe^{2+} + ClO_2 \qquad (8)$$

It was assumed that this step is reversible, and the observed autoinhibition by chlorine dioxide was attributed to the reverse reaction which becomes increasingly important at longer reaction times.

The $[H^+]^{-1}$ dependence of the redox term found in the present study indicates that the initial phase may occur via a different pathway. Under the applied conditions a direct attack by hydroxide ion on the chlorito complex can be excluded. Thus, the rate equation seems to be consistent with a hydrolytic equilibria including $FeClO_2^{2+}$ and presumably $Fe(OH)ClO_2^+$ (reaction 3), which is followed by the decomposition of the latter species.

$$Fe(OH)ClO_2^+ \rightarrow \text{products} \qquad (9)$$

Providing that reaction 9 is rate determining and its rate constant is k_d, $k_r = k_d/K_3$. In general, complex formation reduces the acidity of the metal ion center and $1/K_3$ is expected to be smaller than K_h (5.6×10^{-4} M). On the basis of these arguments, $k_d \geq 152\ s^{-1}$. It also follows that the lack of significant pressure dependence of the rate constant k_r represents a composite kinetic feature. Since only a very uncertain value could be determined for the corresponding activation volume, this aspect is not discussed any further.

Reaction 9 may proceed through iron(II) or iron(IV). Although iron(IV) has not been experimentally detected yet, it was postulated in various redox reactions of aqueous iron species.[29–31] As discussed before,[7,10] the alternative catalytic cycles via Fe(II) and Fe(IV) are equivalent in that they postulate the formation of the same chlorine intermediates according to similar kinetic patterns. If the intermediate is iron(II), it may generate a chlorine(II) species in a fast redox step with chlorite ion.[1] The decomposition of $Fe(OH)ClO_2^{2+}$ via Fe(IV) may produce directly Cl(II). In both cases, the reaction of chlorine(II) with the excess chlorite ion leads to a complex reaction sequence between various chlorine intermediates and chlorite ion. The most important aspects of this mechanism have recently been discussed in detail.[10]

Finally, it should be emphasized that the intermediates are formed at very low concentration levels. Thus, no direct experimental evidence is available to distinguish the two possible pathways via Fe(II) or Fe(IV). The elaboration of a more precise mechanism would require better characterization of the transient species—Cl(II), Cl_2O_2, Cl_2O, and perhaps Fe(IV)—formed in this system.

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Supplementary Material Available: A table of rate constants (2 pages). Ordering information is given on any current masthead page.

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