Suppressed oxygen evolution during chlorate formation from hypochlorite in the presence of chromium(VI)

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Abstract

BACKGROUND: Chromium(VI) is a crucial electrolyte component in industrial chlorate production. Due to its toxicity, it urgently needs to be abandoned and its functions fulfilled by new solutions. In the industrial production of sodium chlorate, homogeneous decomposition of the hypochlorite intermediate to chlorate is a key step. As a competing loss reaction, hypochlorite can decompose to oxygen. How chromium(VI) affects these reactions is not well understood.

RESULTS: This work shows, for the first time, that chromium(VI) selectively accelerates the chlorate formation from hypochlorite both in dilute and concentrated, industrially relevant solutions. The effect of the ionic strength and the specific contribution of different electrolyte components were systematically studied. By simultaneously measuring the concentration decay of hypochlorite (UV–vis spectroscopy) and the oxygen formation (mass spectrometry), both the rate and the selectivity of the reactions were evaluated.

CONCLUSION: In the presence of chromium(VI) the hypochlorite decomposition is described by the sum of an uncatalyzed and a parallel catalyzed reaction, where oxygen only forms in the uncatalyzed reaction. When removing chromium(VI), the homogeneous oxygen formation increases, causing economic and safety concerns. The need for a catalyst selective for chlorate formation is emphasized.

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Supporting information may be found in the online version of this article.

INTRODUCTION

About 95% of the sodium chlorate produced worldwide is used in kraft pulp bleaching.[1] As the use of different paper products is increasing, the demand for sodium chlorate is still growing. The annual production was about 4 million tons in 2017.[2] This amount is almost exclusively produced by the electrolysis of concentrated brine solutions (Eqn (1)), making the chlorate production one of the major electrochemical industrial processes of today.

$$NaCl + 3H_2O \xrightarrow{\text{Electrical energy}} NaClO_3 + 3H_2 \qquad (1)$$
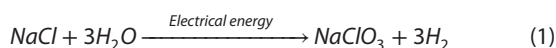
Chromium(VI) is an essential component in the chlorate electrolyte, ensuring high hydrogen evolution selectivity on the cathode.[3–5] As all chromium(VI) species are classified as carcinogenic, mutagenic and reprotoxic (CMR), it has been included in Annex XIV of REACH, and is aimed to be phased out from industrial use. An authorization must now be granted by the European Commission for continued industrial use in Europe and a search for alternatives[6] to chromium(VI) in the chlorate process is therefore of high concern. In this search, it is important to gain a better understanding of the functions of chromium(VI) in the

process.[5] Even though the effect of chromium(VI) on the cathode reactions has been extensively studied,[7–11] less is known about its role in the homogenous decomposition of hypochlorite, and most importantly, the losses due to oxygen formation has not been clarified yet.

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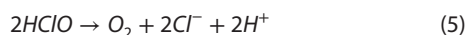
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During the electrolytic process, chlorine produced on the anode dissolves and forms hypochlorite ions and hypochlorous acid (for simplicity, in what follows the term 'hypochlorite' will be used as a general expression for the sum of these species). The chlorate product is formed from hypochlorite according to the overall stoichiometry shown in Eqn (2). The kinetics of the reaction in the absence of chromium(VI) was investigated earlier, and a complex reaction mechanism was proposed.[12] Most importantly, the model describes a fast initiation step between two HClO molecules (or HClO and ClO$^-$). The third molecule (either ClO$^-$ or HClO) reacts in a subsequent, rate-determining reaction step. This model satisfactorily describes the experimentally found third-order kinetics (Eqn (3), where $C_H = [HClO] + [ClO^-]$ and k is the third-order rate constant). Note that in the equations expressed with C_H (instead of [HClO] and [ClO$^-$]) k_1 is the experimental third-order rate constant, which contains the value of pH and pK_a as detailed in the Supporting information in File S1.

$$2HClO + ClO^- \rightarrow ClO_3^- + 2Cl^- + 2H^+ \tag{2}$$

$$\frac{dC_H}{dt} = -k\,[HClO]^2\,[ClO^-] = -k_1 C_H^3 \tag{3}$$

$$2ClO^- \rightarrow O_2 + 2Cl^- \tag{4}$$

$$2HClO \rightarrow O_2 + 2Cl^- + 2H^+ \tag{5}$$

Similarly to the chlorate formation reaction, the decomposition of hypochlorite to oxygen (Eqn (4) and (5)) has been shown to follow third-order kinetics in dilute solutions at pH = 6.5.[13] Its rate is pH dependent, having its maximum at the same pH as the chlorate-forming reaction. It was therefore proposed that these reactions share an intermediate, which can decompose to either oxygen or chlorate.[13] In the absence of catalytic species in the solution, the preferred reaction path is the chlorate formation, and only a minor portion of hypochlorite decomposes to oxygen. The relative rate of these reactions is however strongly affected by the presence of different impurities in the solution.[13–15] Note, that an increased oxygen formation is not only an efficiency loss but also a safety hazard, as when it exits the electrolyzers with the cathodically formed hydrogen (Eqn (1)) explosive gas-mixtures may form. When altering the electrolyte composition in any way, it is therefore important to study the effect on the homogeneous oxygen formation.

A typical industrial chlorate electrolyte contains 500–650 g dm^{-3} NaClO$_3$, 100–120 g dm^{-3} NaCl, 3–8 g dm^{-3} Na$_2$Cr$_2$O$_7$ and 1–3 g dm^{-3} NaClO at T = 70–80 °C and pH = 6–7. An anodic by-product is perchlorate, which although formed at a low rate on the DSA anodes[16,17] can build up to high concentrations over some years in the closed-loop operation.[18] The ionic strength has a significant impact on the hypochlorite decomposition and oxygen formation rate.[19–21] The effect of the chlorate electrolyte components has however not been evaluated systematically under industrially relevant conditions.

Recently, three papers reported on the rate enhancing effect of Na$_2$Cr$_2$O$_7$ addition on the homogeneous decomposition of hypochlorite.[22–24] Regarding the kinetics of the decomposition, Spasojević[23] found that the reaction order with respect to hypochlorite was 3, both in the absence and presence of chromium(VI). Wanngård[22] and Kalmár[24] on the other hand found that in the presence of chromium(VI) the hypochlorite decomposition could be described by the sum of an uncatalyzed third-order reaction, and a parallel catalyzed reaction of order ~2 with respect to hypochlorite. In all studies, chromium(VI) species were included

in the rate expressions. As the rate of oxygen gas formation was not measured in these studies, the lack of clarity concerning the effect of chromium(VI) on this reaction remains.

Here we present an experimental setup for the quantitative investigation of the homogeneous decomposition of hypochlorite. The oxygen formation rate and the hypochlorite concentration change were followed during the reaction at constant solution pH and temperature, hence allowing calculation of the chlorate formation selectivity. Building on our previous work, the decomposition of hypochlorite was first studied in dilute solutions. The effect of the industrial electrolyte constituents was then investigated by gradually increasing the concentrations of sodium chloride, sodium chlorate and sodium perchlorate. Finally, the effect of Na$_2$Cr$_2$O$_7$ addition was studied under controlled, industrially relevant conditions.

MATERIALS AND METHODS
Chemicals
The commercially purchased chemicals were used as received, without further purification. NaClO (0.5 mol dm^{-3} solution in 0.1 mol dm^{-3} NaOH, containing 0.5 mol dm^{-3} NaCl), NaCl (Ph Eur.), NaClO$_4 \cdot$ H$_2$O (ACS grade), NaOH (analytical reagent), acetic acid (GPR Rectapur) and HCl 37% solution (Emsure®) were purchased from VWR International, Spånga, Sweden while KI (pro analysi) and Na$_2$Cr$_2$O$_7$ (pro analysi) were from Merck, Stockholm, Sweden and anhydrous sodium acetate (>99% FCC) from Sigma-Aldrich, Stockholm, Sweden. The sodium chlorate used in our experiments was provided by AkzoNobel and was purified by recrystallization. Commercially available buffer solutions of pH = 4.00 and 7.00 from Metrohm were used to calibrate the pH meter (Metrohm 827 pH lab instrument or Metrohm 907 Titrando titrator equipped with a Unitrode with Pt 1000 combined pH and temperature sensor) prior to each experiment. MilliQ grade ($\rho = 18.2$ MΩ cm, produced by a Millipore Direct–Q3 UV instrument) water was used for preparing all aqueous solutions.

The salts (sodium chlorate, sodium chloride) were dissolved in the reaction chamber at T = 80 °C. Subsequently, the hypochlorite (50 cm^3) was added to the solution to make a total volume of V = 320 cm^3. The sodium perchlorate solutions were prepared similarly, based on literature data.[25]

METHODS
Quantifying the formed oxygen amount
The measurements were performed in a custom-designed setup (see Fig. 1) in which the pH was continuously monitored and regulated (Metrohm 907 Titrator, using 6 mol dm^{-3} HCl and 2 mol dm^{-3} NaOH solutions, equipped with a Unitrode Pt 1000 combined pH and temperature sensor). In this study, 'pH' is defined as the reading from the instrument, after its calibration to the above mentioned commercial buffer solutions. Note that in the very concentrated electrolytes the activity of H$^+$ may have a very different value. The temperature of the solution was measured with the same electrode and was regulated by circulating water from an external heater bath in the jacket of the cell. The concentration of hypochlorite in the solution was followed by taking liquid aliquots and analyzing them by UV–vis spectroscopy (Expedeon VersaWave type instrument). The molar absorbance value of $\varepsilon_{292\,nm} = 350$ dm^3 mol^{-1} cm^{-1} was used for the calculations, which was confirmed by our own calibration experiments (see details in Supporting information in Figure S1 – S3in FIle S1).[26] The
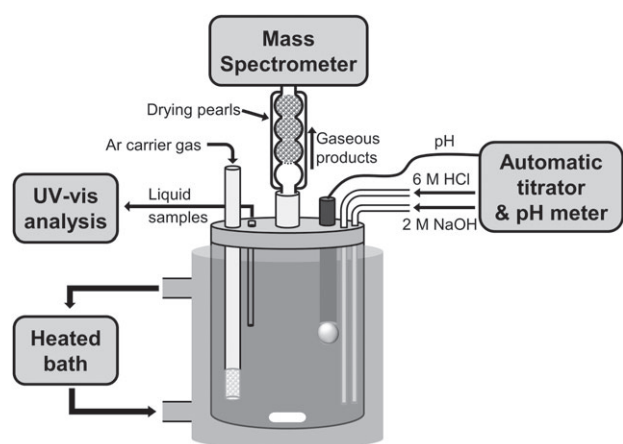
Figure 1. Schematics of the experimental setup used for studying the decomposition of hypochlorite.

sodium chlorate concentration of the solution was not analyzed in this work, as the precision of any applicable analytical method (titration, ion chromatography) is not high enough to reliably detect the small changes in the concentrated solutions (5.2 mol dm^{-3} NaClO$_3$) used in this study (maximum 80/3 mmol dm^{-3} increase, as dictated by the stoichiometry of the hypochlorite decomposition reaction, shown in Eqn (2), and by the initial concentration of hypochlorite, $C_H = 80$ mmol dm^{-3}). Note that in previous work[13] it was shown, that the mass balance during hypochlorite decomposition can be reliably given based on measuring only oxygen or chlorate production rate in relation to hypochlorite concentration decay. The closed reaction vessel (Fig. 1) was continuously purged with argon carrier gas, and the cell off-gas was fed to a mass spectrometer (Hiden HPR-20 type benchtop mass spectrometer, equipped with a quartz capillary inlet) where it was continuously analyzed by monitoring the typical m/z values of the species present.

For a typical measurement, the hypochlorite-containing solution was first heated to 80 °C, while its pH was kept at pH ≈ 12 to minimize the decomposition rate of hypochlorite. During this time, three samples were taken for UV–vis analysis to reliably quantify the initial hypochlorite concentration. Subsequently, the reaction was initiated by adding a predetermined volume of 6 mol dm^{-3} HCl to reach pH = 6.5, which was then kept constant during the measurements. Further details can be found in the Supporting information in File S1).

Quantifying the desorption of hypochlorous acid

The desorption of hypochlorous acid from the solution during the reaction was also investigated, see details in the Supporting information in File S1. The extent of this loss depends on the ionic strength - in the dilute solution (80 mmol dm^{-3} hypochlorite +80 mmol dm^{-3} NaCl) it is less than 0.2%, while in the case of the most concentrated solution studied in this work it is around 1.5% of the decomposed hypochlorite amount during a 60 min long measurement (Supporting information Fig. S4 and S5 in File S1). These losses were neglected in our further analysis.

RESULTS AND DISCUSSION
The effect of chromium(VI) on hypochlorite decomposition in dilute solutions

The rate and selectivity of hypochlorite decomposition was first studied in dilute solutions (80 mmol dm^{-3} hypochlorite
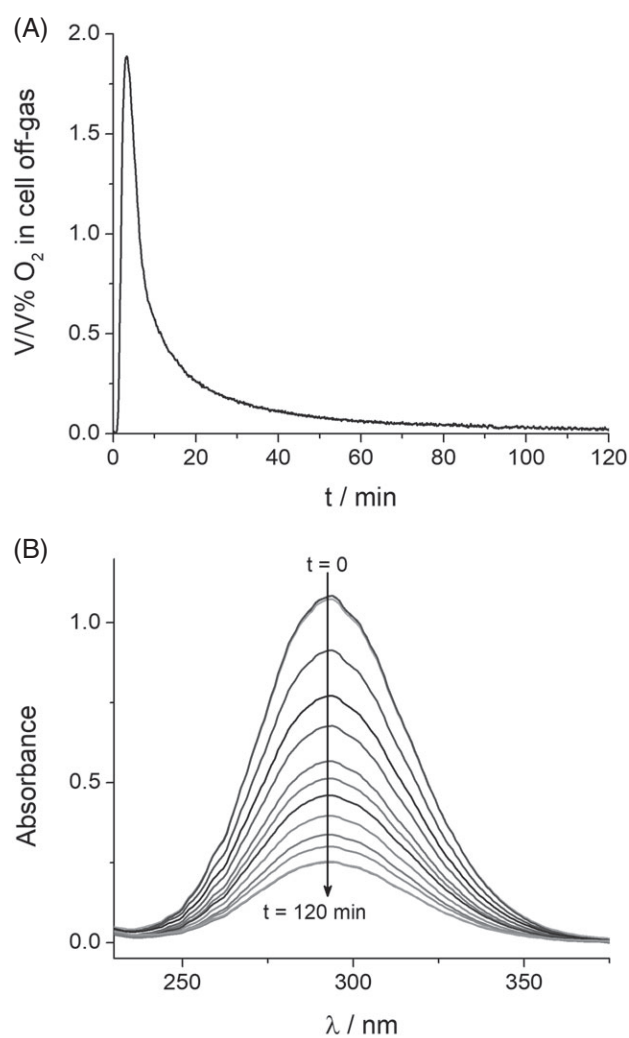

Figure 2. (A) Oxygen content of the cell off-gas, as detected by the mass spectrometer, and (B) UV–vis spectra recorded during a hypochlorite decomposition reaction in an 80 mmol dm^{-3} NaClO solution at pH = 6.5 and T = 80 °C.

+80 mmol dm^{-3} NaCl) without any further additives. The oxygen formed was quantified by continuously analyzing the cell off-gas using mass spectrometry (Fig. 2(A)), while the concentration of hypochlorite in the solution was monitored by UV–vis spectroscopy (Fig. 2(B)). At the beginning of the recorded oxygen evolution rate curve a delay time of 2–3 min was observed. This can be attributed to the geometry of the setup, as a dead volume is formed by the headspace over the solution and by the volume of the tubing connecting the cell to the mass spectrometer. Although this makes it difficult to extract kinetic information from the oxygen evolution curves, it does not affect the quantification of the total amount of formed oxygen.

The kinetics of the hypochlorite decomposition reaction was analyzed from the hypochlorite concentration decay curves (Fig. 3(A)) calculated from the UV–vis measurements (Fig. 2(B)). In good agreement with our previous results, under these conditions the decomposition reaction follows third-order kinetics with respect to hypochlorite as indicated in Eqn (3) (in the model $k_1 = km = k \frac{10^{pH-pK_a}}{(1+10^{pH-pK_a})^3}$, further explained in the Supporting information in File S1).[13] The fitted experimental rate constant of

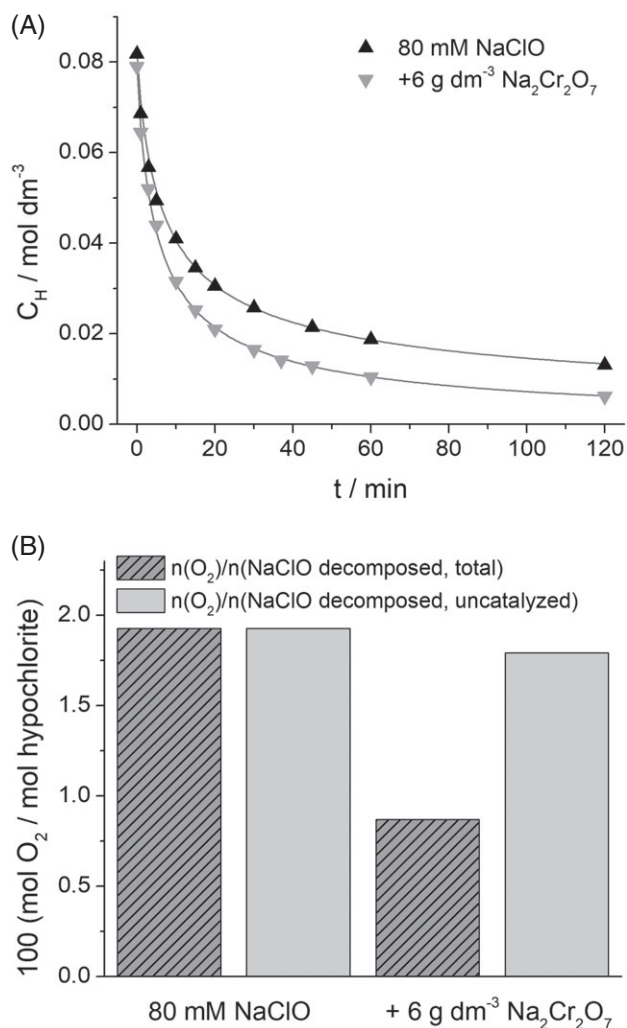**Figure 3.** (A) Concentration decay of hypochlorite in 80 mmol dm^{-3} NaClO solution at pH = 6.5 and T = 80 °C, with and without the addition of 6 g dm^{-3} Na$_2$Cr$_2$O$_7$. The symbols represent the measured data points, while the solid lines show the fitted curves. (B) Ratio of the total amounts of oxygen formed and decomposed hypochlorite over a 120 min reaction period. The molar amount of hypochlorite decomposed in the uncatalyzed reaction was calculated after fitting the k_1 and k_2 rate constants. Details of the calculations can be found in the Supporting information in File S1.

the reaction is $k_1 = 0.38$ dm^6 mol^{-2} s^{-1}. Using the acid dissociation constant of hypochlorous acid ($pK_a = 6.93$), k was calculated to be 2.6 dm^6 mol^{-2} s^{-1}, which coincides well with earlier results.[13]

When adding 6 g dm^{-3} Na$_2$Cr$_2$O$_7$ to the solution, a large increase in the reaction rate was observed (Fig. 3(A)). Importantly, the decomposition rate no longer follows the third-order kinetic model, involving only hypochlorite species as reactants. Instead, in agreement with previous literature data,[22,24] the hypochlorite decomposition rate $\left(r = -\frac{dC_H}{dt}\right)$ can be described by the sum of an uncatalyzed third-order reaction $\left(r_1 = k_1 C_H^3\right)$, and a parallel catalyzed reaction $\left(r_2 = k_2 C_H^\alpha\right)$ (Eqn (6), further detailed in the Supporting information in File S1). Using this model, the experimental data was fitted to give a partial order of $\alpha = 2$, with respect to hypochlorite species, in the second term.

$$\frac{dC_H}{dt} = -\left(k_1 C_H^3 + k_2 C_H^\alpha\right) = -\left(r_1 + r_2\right) \qquad (6)$$

The total amount of oxygen formed during the reaction was calculated by integrating the oxygen evolution rate curves (Fig. 2(A)). To evaluate the selectivity of the reaction, this amount was divided by the total amount of decomposed hypochlorite (Fig. 3(B), columns with hatched pattern). As shown in Fig. 3(B), the oxygen formation ratio is decreased by *c.* 70% upon the addition of chromium(VI). Beyond its effect on the overall reaction rate, the presence of 6 g dm^{-3} Na$_2$Cr$_2$O$_7$ in the solution hence also leads to an increased selectivity towards chlorate formation. After fitting the k$_1$ and k$_2$ values, the contribution of the two competing reaction paths to the overall hypochlorite decomposition can be calculated (see Supporting information Fig. S8A in File S1). The ratio of the total formed oxygen amount and the hypochlorite amount decomposed in the uncatalyzed reaction (Fig. 3(B), columns without pattern) agrees well with what was measured in the absence of the chromium(VI) additive. In other words, the total amount of the formed oxygen can be accounted for by assuming that oxygen is formed only in the uncatalyzed reaction, in the same ratio as in the additive free case. This indicates that in the chromium(VI) catalyzed reaction no, or a negligible amount of oxygen is formed.

The effect of ionic strength on hypochlorite decomposition

The effect of the ionic strength on the rate and selectivity of hypochlorite decomposition was studied by gradually increasing the NaCl and/or NaClO$_3$ concentration until reaching a composition close to the industrial chlorate electrolyte (5.2 mol dm^{-3} (550 g dm^{-3}) NaClO$_3$ + 1.9 mol dm^{-3} (110 g dm^{-3}) NaCl) (Fig. 4(A)). In accordance with what is reported in the scientific literature,[19-21] the decomposition rate of hypochlorite increases with increasing ionic strength. Comparing the hypochlorite concentration decay curves at the same ionic strength set by the two different salts (NaClO$_3$ or NaCl) no significant differences can be observed. This suggests that these salts have no catalytic effect on the reaction, the increased decomposition rate is caused only by the higher ionic strength.

Just as in the case of the dilute hypochlorite solution, the decomposition follows third-order kinetics. This can be seen from the linearity of the data when C_H^{-2} is plotted as a function of time, according to the integrated form of the third-order kinetic expression. The fitted third-order rate coefficients (k_1) can be found in Supporting information Table S1 in File S1. It is important to note that these values are only valid for the experimental conditions used in this study, as these depend on both the pH of the solution and the deprotonation constant of hypochlorous acid.[13] Using the literature value of $pK_a = 6.79$ measured in high temperature high ionic strength solutions, the value of k was calculated from k$_1$ (as detailed in the Supporting information in File S1), and good agreement was found between our result and those reported earlier for ~7 mol dm^{-3} ionic strength solutions (12.8 vs 13.1 mol^{-2} dm^6 s^{-1}).[22]

The selectivity of the reaction is also affected, as a more pronounced oxygen evolution can be observed in solutions of higher ionic strength (Fig. 4(B)). Again, the ratio of the evolved oxygen to the decomposed hypochlorite amount is the same (within experimental error) for the different solutions with the same ionic strength.

Experiments using NaClO$_4$ resulted in similar conclusions, namely that both the rate of hypochlorite decomposition (Supporting information Fig. S7A in File S1), and the oxygen formation ratio (Supporting information Fig. S7B in File S1) increase with ionic strength. The fitted third-order rate constants are however
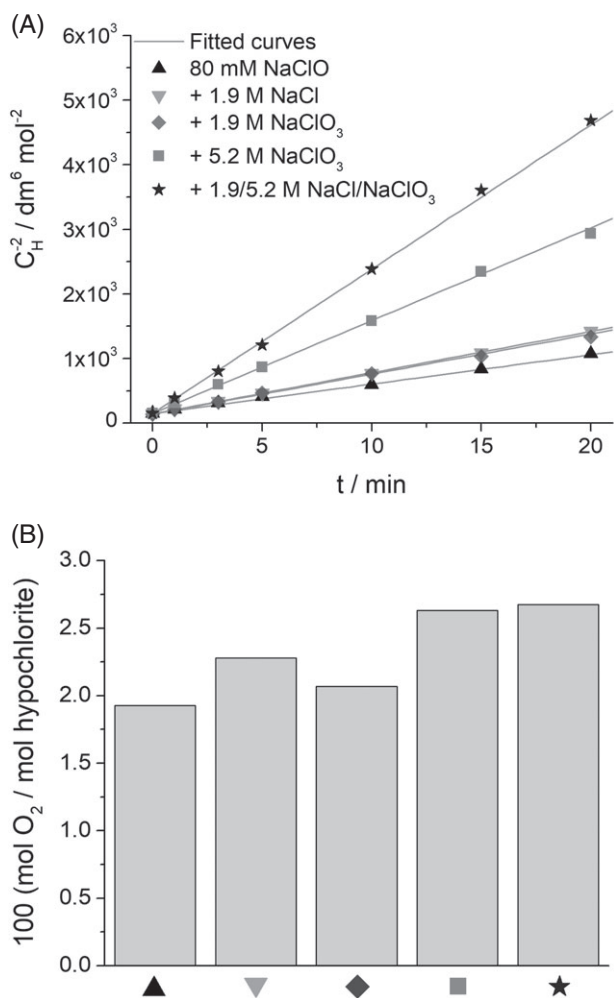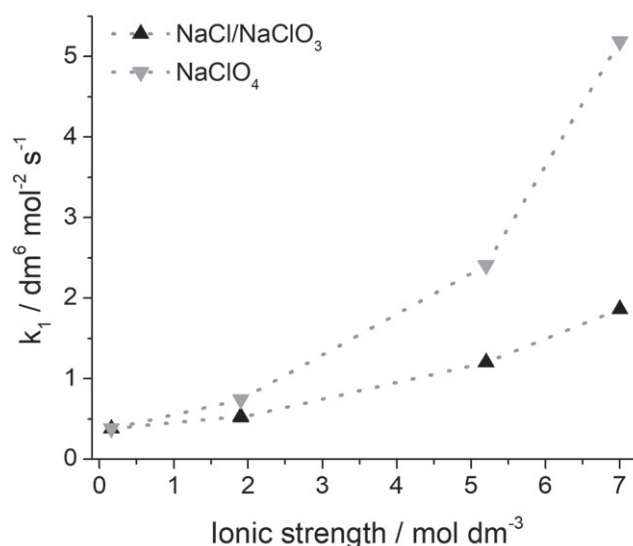
Figure 5. Third-order rate constants evaluated from measurements shown in Fig. 4(A) and supporting information Fig. S7A in File S1.

Hence a limited access to available water may have an inhibiting effect on the rate of this reaction.

The effect of chromium(VI) on hypochlorite decomposition in concentrated solutions

The effect of $Na_2Cr_2O_7$ addition was studied in 5.2 mol dm^{-3} $NaClO_3$ + 1.9 mol dm^{-3} NaCl solutions (Fig. 6). The decomposition rate increases with increased amount of chromium(VI) in the solution (Fig. 6(A)). Similarly to the case of the dilute solution, the decomposition curve in the presence of $Na_2Cr_2O_7$ cannot be fitted by a single third-order term including hypochlorite species only. This is readily seen from the deviation of the data from the linear trend when C_H^{-2} is plotted as a function of time (according to the integrated form of the third-order kinetic expression). Instead, the previously shown kinetic model, (Eqn (6)), describes the curve satisfactorily. For these fittings the k_1 value from the measurements without chromium(VI) addition was used, while k_2 was fitted. Just as in the case of the dilute electrolyte, $\alpha \approx 2$ was found from the fittings, and therefore this value was used to calculate the curves presented in Fig. 6(A). Plotting the logarithm of the fitted k_2 values as a function of the logarithm of the $Na_2Cr_2O_7$ concentration (Supporting information Fig. S6 in File S1), a partial order of ~1.5 was determined for $Na_2Cr_2O_7$.

As seen from the decreasing ratio of oxygen formed to the total amount of decomposed hypochlorite (Fig. 6(B), columns with hatched pattern), the selectivity of the reaction towards chlorate formation increases continuously with increasing concentration of $Na_2Cr_2O_7$. At the typical industrial concentration of 6 g dm^{-3}, the total formed oxygen amount is 0.8% of the decomposed hypochlorite amount, a 70% decrease compared with the chromium(VI)-free case (2.7%). Calculating the contribution of the two competing reaction paths, the amount of hypochlorite decomposed in the uncatalyzed reaction was quantified (supporting information Fig. S8B,C in File S1). The ratio of this and the total amount of formed oxygen (Fig. 6(B), columns without pattern) agrees well at all concentrations with what was measured in 5.2 mol dm^{-3} $NaClO_3$ + 1.9 mol dm^{-3} NaCl containing solutions, in the absence of the chromium(VI) additive. Again, this indicates that in the chromium(VI) catalyzed reaction no, or a negligible

Figure 4. (A) Concentration decay of hypochlorite in solutions of different ionic strength in a solution containing 80 mmol dm^{-3} NaClO at pH = 6.5 and T = 80 °C. The symbols represent the measured data points, while the solid lines show the curves fitted to these. (B) The ratio of the total amounts of formed oxygen and decomposed hypochlorite over a 120 min reaction time. The symbols on the x-axis represent the corresponding measurement from (A).

significantly higher when the same ionic strength is set by $NaClO_4$ instead of $NaClO_3$ and/or NaCl (Fig. 5 and supporting information Table S1 in File S1). This is indeed a very interesting effect, especially since $NaClO_4$ is an unwanted by-product in the process.[18] The reason behind this increased reaction rate is not fully understood yet. Note however, that contrary to ClO_4^-, both Cl^- and ClO_3^- ions are products in the hypochlorite decomposition reaction (Eqn (2)). Any equilibrium reaction steps before the rate limiting step in the reaction scheme involving Cl^- and/or ClO_3^- may influence the reaction rate. Another source of this difference might be found in the different interaction of the perchlorate and chlorate ions with water. Both the chlorate and perchlorate are weakly hydrated ions, while chlorate has a larger hydration shell due to its stronger hydrogen bonds to water.[27] As the ionic strength is getting very high, there might be a significant difference in available water in chlorate/chloride electrolyte compared with perchlorate electrolyte, where ion paring might play an important role. In reaction (2) more species form (ClO_3^-, Cl^-, H^+) than react (HClO, ClO^-) requiring larger amounts of water for the hydration.
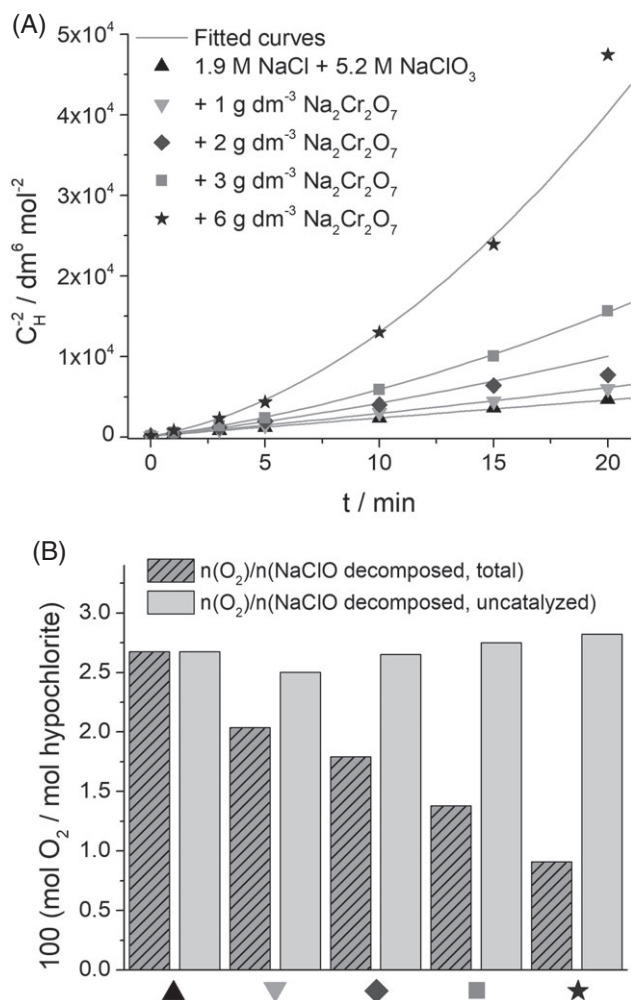
Figure 6. (A) Concentration decay of hypochlorite in an 80 mmol dm^{-3} NaClO containing 5.2 mol dm^{-3} NaClO$_3$ + 1.9 mol dm^{-3} NaCl solution at pH = 6.5 and T = 80 °C, with the addition of Na$_2$Cr$_2$O$_7$ in different concentrations. The symbols represent the measured data points, while the solid lines show the curves fitted to these. (B) Ratio of the total amounts of oxygen formed and decomposed hypochlorite over a 120 min reaction period. The symbols on the x-axis represent the corresponding measurement from (A). Molar amount of hypochlorite decomposed in the uncatalyzed reaction was calculated after fitting the k$_1$ and k$_2$ rate constants. Details of the calculations can be found in the Supporting information in File S1.

amount of oxygen is formed. Further, the constant ratio (2.7%) of the oxygen formed to the amount of hypochlorite decomposed in the uncatalyzed reaction path indicates that the oxygen formation reaction also follows third-order kinetics with respect to hypochlorite species; this ratio is thus independent of the hypochlorite concentration. This corroborates our previous hypothesis, namely that the hypochlorite decomposition to chlorate or oxygen share an intermediate in the reaction scheme during or after the rate determining step.[13]

$$ClO^- + Cl_2O \cdot H_2O \rightarrow HClO + HCl_2O_2^- \qquad (7)$$

$$CrO_4^{2-} + Cl_2O \cdot H_2O \rightarrow HCrO_4^- + HCl_2O_2^- \qquad (8)$$

In the reaction scheme proposed earlier for the uncatalyzed case,[12] the rate-determining reaction (Eqn (7)) proceeds via a transition state complex, formed by a hypochlorite ion and

a Cl$_2$O · H$_2$O molecule. In the reaction scheme suggested by Kalmár[24] for the catalyzed case (Eqn (8)), chromate takes the place of the hypochlorite ion in the transition state. In a chromium(VI)-containing electrolyte the uncatalyzed and catalyzed reactions proceed in parallel. Hence, we assume, that in the presence of chromium(VI) both transition state complexes form in a concentration ratio dependent on the chromium(VI) concentration. The contribution of the uncatalyzed reaction path, and the formation of oxygen decreases simultaneously with the increasing chromium(VI) concentration. This suggests that the oxygen formation proceeds only through the complex formed in Eqn (7), as summarized in Scheme 1.
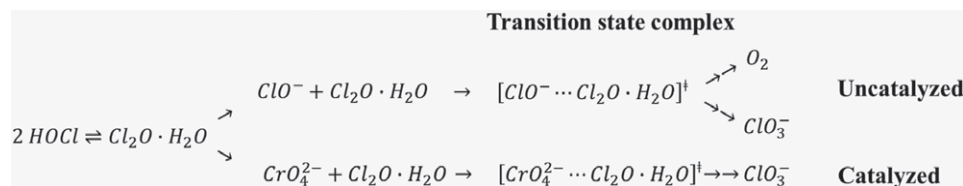
Industrial impact of the results

In industrial chlorate electrolytes the Na$_2$Cr$_2$O$_7$ concentration is typically kept in the range 3–8 g dm^{-3} and, according to industrial experience, the steady-state hypochlorite concentration in the electrolyzer remains in the range of 1–3 g dm^{-3} (25–40 mmol dm^{-3}). As shown in Fig. 7, calculated from the experimentally determined rate constants (Supporting information Table S1 in File S1), with decrease of the hypochlorite concentration and/or increase in chromium(VI) concentration the contribution of the catalyzed route (r$_2$) to the overall decomposition rate (r = r$_1$ + r$_2$) of hypochlorite becomes increasingly important. At industrially relevant conditions the chromium(VI) catalyzed decomposition of hypochlorite is dominant. As no oxygen seems to be formed in this step, the chromium(VI) additive in the solution contributes to the overall efficiency of the chlorate synthesis by lowering the homogeneous formation of the oxygen by-product. Also, the low steady-state hypochlorite concentration leads to moderate anodic oxygen formation from hypochlorite.

In the absence of chromium(VI) the decomposition rate will decrease, and the steady-state hypochlorite concentration will therefore increase. This will cause an increased formation of oxygen from anodic reactions in addition to the important homogeneous oxygen formation. As earlier mentioned, the overall hypochlorite decomposition and both the oxygen and chlorate formation reactions are of third order with respect to hypochlorite species. This implies that the selectivity between oxygen and chlorate in the homogeneous reactions is independent of hypochlorite concentration.

Hypochlorite and hydrogen forms in the same rate in a chlorate cell, as shown by the cathodic and anodic half-cell reactions and the hydrolysis equilibrium of chlorine (Eqns (9)–(11)).

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (9)$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (10)$$

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl \qquad (11)$$

During the steady-state operation there is no hypochlorite accumulation, the rate of hydrogen production and hypochlorite decomposition are equal. The constant oxygen formation to hypochlorite decomposition ratio would thus mean that the uncatalyzed homogeneous decomposition of hypochlorite may contribute to the O$_2$ content of the off-gas with up to 2.7 V/V%, as dictated by the formed oxygen/decomposed hypochlorite ratio of 0.027. In the currently applied cell configurations the oxygen content of the off-gas is typically 2–3 V/V% in the presence of chromium(VI), where the majority of hypochlorite decomposes through the catalyzed reaction (Fig. 7). According to our results,

Transition state complex

$$2\,HOCl \rightleftharpoons Cl_2O \cdot H_2O$$

$$ClO^- + Cl_2O \cdot H_2O \rightarrow [ClO^- \cdots Cl_2O \cdot H_2O]^{\ddagger} \begin{array}{c} \nearrow O_2 \\ \searrow ClO_3^- \end{array} \quad \textbf{Uncatalyzed}$$

$$CrO_4^{2-} + Cl_2O \cdot H_2O \rightarrow [CrO_4^{2-} \cdots Cl_2O \cdot H_2O]^{\ddagger} \rightarrow ClO_3^- \quad \textbf{Catalyzed}$$

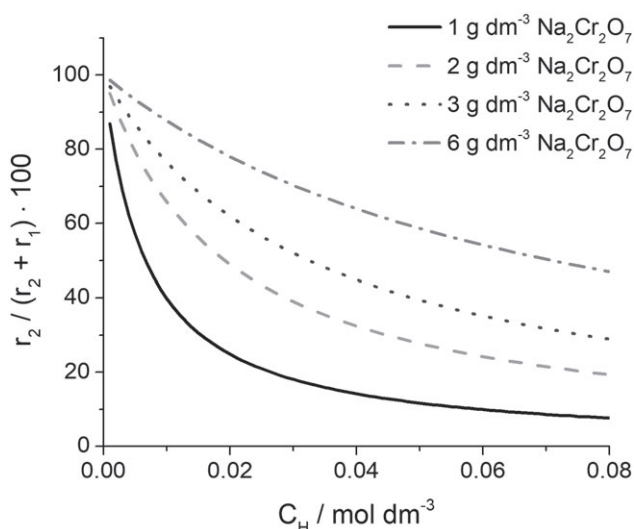**Scheme 1.** Proposed reaction mechanism for the catalyzed and uncatalyzed hypochlorite decomposition reactions.

Figure 7. Ratio of the rate of catalyzed to the overall decomposition rate of hypochlorite at different NaClO concentrations in 5.2 mol dm^{-3} NaClO$_3$ + 1.9 mol dm^{-3} NaCl solutions (pH = 6.5 and T = 80 °C) with different Na$_2$Cr$_2$O$_7$ concentrations. The data was calculated according to Eqn (6), using the rate constants fitted to the measurements shown in Fig. 4 and Fig. 6).

this oxygen is not formed during hypochlorite decomposition, but most probably comes from the anodic reaction. In the absence of chromium(VI) all hypochlorite would decompose through the uncatalyzed reaction, which could, depending on the process configuration, increase the oxygen level of the cell off-gas above the explosion limit.

As the chromium(VI) additive must be replaced in the chlorate process according to the decision of the European Commission, finding a catalyst selective for chlorate formation is crucial for the safe and sustainable operation of the current chlorate producing plants. As our results emphasize - for the first time - the homogeneous oxygen formation must be taken into consideration when evaluating the potential candidates to replace chromium(VI).

CONCLUSIONS

In this study the decomposition of hypochlorite was investigated in solutions of different ionic strength and Na$_2$Cr$_2$O$_7$ concentration. By simultaneously measuring the concentration decay of hypochlorite (UV–vis spectroscopy) and the formed oxygen amount (mass spectroscopy), both the rate and the selectivity of the reaction was evaluated.

In the absence of Na$_2$Cr$_2$O$_7$, the decomposition reaction follows third-order kinetics with respect to hypochlorite, irrespective of the ionic strength of the solution. When adding Na$_2$Cr$_2$O$_7$ to the solution, the decomposition can however no longer be described

by this model. Instead, the competition between two reactions (a catalyzed, involving chromium(VI) as a reactant, and an uncatalyzed, involving only hypochlorite species) is proposed in agreement with the results of previous works. The rate of decomposition increases both with ionic strength and chromium(VI) concentration. The increased ionic strength leads to a more pronounced oxygen formation, and hence to increased losses in the industrial process. When the ionic strength is set by NaClO$_4$, the increase in reaction rate is significantly higher than when using NaClO$_3$ and/or NaCl. On the other hand, the selectivity of the reaction is the same at any given ionic strength for these two background electrolytes. The Na$_2$Cr$_2$O$_7$ addition increases the rate of hypochlorite decomposition and leads to a significantly increased selectivity towards chlorate formation. Analyzing the contribution of the two parallel reactions in the Na$_2$Cr$_2$O$_7$ containing solutions, the results indicate that no, or a negligible amount of oxygen is formed in the chromium(VI) catalyzed decomposition reaction.

Because of the increasing health and safety concerns, the chromium(VI) additive must soon be removed from the industrial process. This would lead to increased oxygen formation, in particular from homogeneous hypochlorite decomposition, which would not only affect the process efficiency but would also constitute a safety hazard due to risk of explosions. Finding a selective catalyst for chlorate formation from hypochlorite decomposition is highly important for a chromium(VI)-free chlorate process.

Supporting Information

Supporting information may be found in the online version of this article.

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