



Tertiary amine-catalyzed generation of chlorine dioxide from hypochlorous acid and chlorite ions

Estefania Isaza Ferro¹ · Jordan Perrin¹ · Owain George John Dawson¹ · Tapani Vuorinen¹

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Abstract

The reaction between hypochlorous acid and chlorite ions is the rate limiting step for in situ chlorine dioxide regeneration. The possibility of increasing the speed of this reaction was analyzed by the addition of tertiary amine catalysts in the system at pH 5. Two amines were tested, DABCO (1,4-diazabicyclo[2.2.2]octane) and its derivative CEM-DABCO (1-carboethoxymethyl-1-azonia-4-aza-bicyclo[2.2.2]octane chloride). The stability of the catalysts in the presence of both reagents and chlorine dioxide was measured, with CEM-DABCO showing to be highly stable with the mentioned chlorine species, whereas DABCO was rapidly degraded by chlorine dioxide. Hence, CEM-DABCO was chosen as a suitable candidate to catalyze the reaction of hypochlorous acid with chlorite ions and it significantly increased the speed of this reaction even at low catalyst dosages. This research opens the door to a faster regeneration of chlorine dioxide and an improved efficiency in chlorine dioxide treatments.

Introduction

Tertiary amines are versatile compounds that can catalyze a wide range of organic (Ammer et al. 2010) and oxidation reactions (Prütz 1998; Huang and Shah 2018). They are versatile catalysts because of their nucleophilic character and their availability to incorporate different functional groups, which may provide higher stability and reactivity (Prütz 1998; Shah et al. 2011; Dodd et al. 2005). Tertiary amines can be used as catalysts in polyurethane production (Sardon et al. 2015), in the Baylis–Hillman reaction, enhancing the generation of new C–C bonds (Basavaiah et al. 2010) and in water treatment. In water treatment, tertiary amines have been shown to boost the degradation of organic contaminants and promote the disinfection of

✉ Estefania Isaza Ferro
estefania.isazaferro@aalto.fi

¹ Department of Bioproducts and Biosystems, Aalto University School of Chemical Engineering, P.O. Box 16300, 00076 Espoo, Finland

water (Huang and Shah 2018; Basavaiah et al. 2010). It is known that the addition of a tertiary amine such as DABCO (1,4-diazabicyclo[2.2.2]octane) to hypochlorous acid (HOCl) produces a highly reactive chlorommonium cation (Rosenblatt et al. 1972). This chloroammonium cation can oxidize saturated structures faster than HOCl (Afsahi et al. 2015; Prütz 1998). Hence, many industries could benefit from faster reactions using chloroammonium cations, including energy-intensive pulp bleaching processes. Nevertheless, finding the right structure that would be stable with the chlorine species, and especially with HOCl and chlorine dioxide (ClO_2), has proven challenging.

HOCl is a strong oxidant that exists in a pH-dependent equilibrium with chlorine (Cl_2) and hypochlorite ion (ClO^-). At pH higher than the pKa (7.6) of HOCl, ClO^- ion is the dominant species, while at $\text{pH} < 3.5$, the presence of Cl_2 becomes significant. Between these points, HOCl is the most abundant and important species (Gombas et al. 2017). Although HOCl and Cl_2 are efficient oxidants, they have been displaced by ClO_2 in some applications because ClO_2 produces lower amounts of organochlorinated compounds than elemental chlorine chemicals (Cl_2 , HOCl and ClO^-) do (Prütz et al. 2001).

ClO_2 is a strong oxidant that is widely used in industrial pulp bleaching (Sixta et al. 2006; Gordon and Rosenblatt 2005) and water disinfection (Ye et al. 2019; Benisti 2018). ClO_2 is produced on site because it cannot be stored or transported due to its toxicity and instability. It is usually produced from sodium chlorate (Gordon and Rosenblatt 2005), but it can also be produced from the reaction of sodium chlorite ions and sodium hypochlorite in acidic conditions (Masschelein 1967). More interestingly, chlorine dioxide can be regenerated, meaning that its degradation products can react to reform chlorine dioxide. This is the case in the oxidation of organic phenolic substrates, where chlorine dioxide is reduced to hypochlorous acid (HOCl) and chlorite ions (ClO_2^-) (Svenson et al. 2006), which react together, forming ClO_2 again. The importance of the reaction of HOCl with ClO_2^- derives from its role in the regeneration of ClO_2 (Fig. 1), but it may also be the key to a lowered production of organochlorinated compounds. ClO_2 treatments produce a low amount of organochlorinated compounds and it is believed that the small percentage formed is caused by the reactions of the in situ formed HOCl and Cl_2 (Kolar et al.

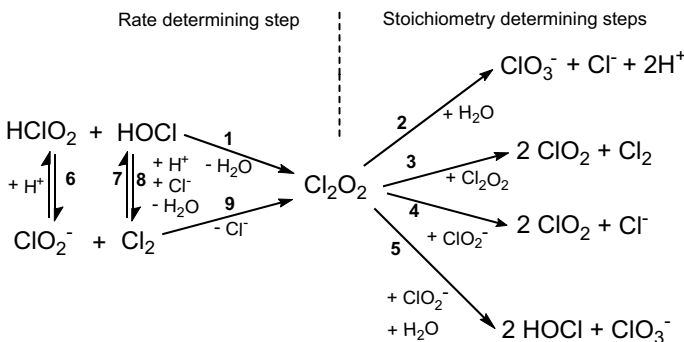


Fig. 1 Schematic representation of the reaction between HOCl and ClO_2^- (Tarvo et al. 2009)

1983; Lehtimaa et al. 2010; Gallard and von Gunten 2002). Hence, finding a catalyst that increases the reaction rate of the rate determining step in ClO_2 regeneration is one possibility to push the equilibrium toward higher amounts of ClO_2 , and therefore to reduce the available HOCl that would be able to react with organic substrates.

Tertiary amines are a clear option to catalyze the regeneration reaction of ClO_2 . They are more available and less expensive than transition metals, which yield a high conversion of ClO_2^- into ClO_2 in acidic conditions (Ringo 1991; Hardee et al. 1983). However, tertiary amines are known to be unstable, especially in the presence of chlorine dioxide. For example, the DABCO chloroammonium cation is unstable by itself, and it undergoes oxidative fragmentation (Brennesein et al. 1965) via carbon–carbon cleavage, producing 1-4-dichloropiperazine, formaldehyde and chloride (Dennis et al. 1967; Fig. 2). A similar oxidative degradation takes place when the DABCO chloroammonium cation is exposed to ClO_2 , producing piperazine, ammonia and formaldehyde (Dennis et al. 1967). Previous research has shown that formaldehyde can react with chlorous acid (HClO_2), regenerating ClO_2 (Jiang et al. 2007; Ventorim et al. 2005). However, this reaction also generates undesired formic acid and hydrochloric acid. In summary, the addition of DABCO likely improves the regeneration of ClO_2 by the formation of both the chloroammonium cation and of formaldehyde, but it also consumes oxidative power in later degradation stages. Hence, finding a tertiary amine that is stable in aqueous ClO_2 and HOCl is fundamental for their potential use in ClO_2 treatments.

Recently, an alkyl-substituted DABCO derivative called CM-DABCO was used to generate an active but stable chloroammonium cation in the presence of HOCl at pH 5 (Afsahi et al. 2019). Hence, alkyl-substituted DABCO derivatives appear to have a larger potential in the catalysis of the chlorine dioxide regeneration reaction. It is expected that CEM-DABCO, just like DABCO, will form a chloroammonium cation with HOCl (Fig. 2). However, the stability of both chloroammonium cations is predicted to differ greatly. The chloroammonium cation of DABCO, is an unstable structure, whereas the chloroammonium cation of CEM-DABCO is expected to be stable. It has no lone pair of electrons due to the alkyl substitution in one of the amino positions, and hence, it will not undergo intramolecular fragmentation.

This article aims to break the old paradigm that tertiary amines are no suitable catalysts in the presence of ClO_2 and to study the impact of two tertiary amines in the chlorine dioxide regeneration reaction. The two chosen catalysts

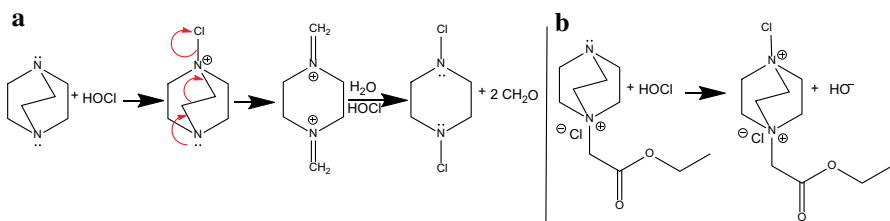


Fig. 2 a Formation and degradation of chloroammonium cation from DABCO (Dennis et al. 1967). b Formation of CEM-DABCO chloroammonium cation that does not degrade because it lacks the required free electron pair on nitrogen atom

are DABCO (as a reference case) and an n-alkyl-substituted DABCO catalyst, hereinafter referred to as CEM-DABCO (1-carboethoxymethyl-1-azonia-4-azabicyclo[2.2.2]octane chloride). CEM-DABCO is an intermediate species in CM-DABCO synthesis; hence, it is easier to synthesize. It should display similar stability and catalytic activity to CM-DABCO because it also has one available amino group to form the chloroammonium cation and a low-impact group (alkyl substitution) in the second amino group.

This article will first identify the optimum pH at which the CEM-DABCO chloroammonium cation is formed, before studying the stability of CEM-DABCO in the ClO_2 regeneration system. Finally, it will assess the overall impact of CEM-DABCO in the reaction of HOCl with ClO_2^- . The impact of a more stable, but still active, tertiary amine catalyst in the reaction of HOCl with ClO_2^- could translate into more efficient ClO_2 treatments with lowered initial chemical charges and energy consumptions. Additionally, it could result in a cleaner treatment, with lowered amounts of organochlorinated compounds produced.

Materials and methods

Materials

Fast kinetics experiments

Commercial sodium hypochlorite (NaOCl) solution and pH 5 buffer solution (citric acid/sodium hydroxide) were purchased from VWR. The NaOCl purity was 7.3% and contained ClO_3^- (3.7%) and ClO_2 (0.2%) as impurities. Chlorine dioxide (ClO_2) was produced in a Denzo reactor at 65 °C via the mixing of 1000 g of pure oxalic acid (Merck), 265 g of pure potassium chlorate (Sigma-Aldrich) and 1000 ml of distilled water. Solid sodium chlorite (NaClO_2) (80%) was also acquired from Sigma-Aldrich. Aqueous solutions of NaOCl, NaClO_2 and ClO_2 were prepared and titrated daily for determination of their active chlorine concentrations. The tertiary amine catalyst, DABCO (1,4-diazabicyclo[2,2,2]octane) (99%), was purchased from Sigma-Aldrich.

The tertiary amine, CEM-DABCO (1-carboethoxymethyl-1-azonia-4-azabicyclo[2.2.2]octane chloride), was synthesized (Engel et al. 2009) by dissolving DABCO (1.222 g) in 20 mL of ethyl acetate, and adding dropwise ethyl chloroacetate on the stirred solution, both purchased from Sigma-Aldrich. The solution was left to react for 1 h; the resulting white precipitate was washed 3 times with 30 ml of ethyl acetate and later vacuum-dried to produce CEM-DABCO as a white solid (1.9 g, 74%). ^1H NMR (400 MHz, D_2O): δ_{H} 1.20 (3H, t, $^3J_{\text{HH}}=7.2$, $\text{COOCH}_2\text{CH}_3$); 3.16 [6H, t, $^3J_{\text{HH}}=7.6$, $(\text{CH}_2)_3 \text{N}^+$]; 3.59, [6H, t, $^3J_{\text{HH}}=7.6$, $(\text{CH}_2)_3 \text{N}$]; 4.17 (2H, s, $\text{N}^+\text{CH}_2\text{COOEt}$); 4.21 (2H, q, $^3J_{\text{HH}}=7.2$, $\text{COOCH}_2\text{CH}_3$). ^{13}C NMR (400 MHz, D_2O): 13.10, 43.97, 52.79, 61.67, 63.42, 164.70.

Iodometric titrations

Titanium (II) chloride solution ($\geq 12\%$) was procured from Sigma-Aldrich. Hydrochloric acid (37%), sulfuric acid (1 M), sodium thiosulfate pentahydrate and potassium iodide were purchased from VWR.

Methods

Fast kinetics experiments

The chemical reactions were conducted using the stopped flow mixer Bio-Logic SFM-3000 and an ASPEN TIDAS array spectrophotometer. The SFM-3000 reactor allows the precise injection and mixing of small amounts (μl range) of reagents. The mixed solution passes into a Quartz cuvette, with 1.5 mm of light path length, where it is exposed to the light of a xenon mercury lamp. The absorbance information of the solution is collected at every fraction of a second, between the wavelength of 180 and 800 nm. The data were processed using the software Bio-Kine32 version 4.64.

The Bio-Logic SFM-3000 reactor was used to follow the stability of the catalysts and their impact on the reaction of hypochlorous acid with chlorite ions. The experiments were performed at 25 °C and pH 5 since there is evidence that in these conditions the chloroammonium cation of DABCO presents good oxidation results (Afsahi et al. 2015). The molar mixing proportions were 1:1:1 in all the cases, except for the catalyst dosage experiment. The initial concentration of the reagents in the mixed solution was approximately 5 mM, and the real concentration values of the reagents inside the cuvette were calculated using Beer's law equation and the measured absorbance values. The error for this technique is $\pm 5\%$ of the measured absorbance value. Table 1 presents the molar absorptivity values (ϵ) for HOCl, ClO_2^- and ClO_2 which were taken from previous literature (Körtvélyesi 2004) and mostly confirmed within the current experiments. The only value that differed from the literature was the ϵ of chlorine dioxide at 235 nm. The value proposed by Körtvélyesi ($167 \text{ M}^{-1} \text{ cm}^{-1}$) delivered amounts of ClO_2 that did not correspond to the titration results nor the calculated ClO_2 quantities using the measured absorbances at ϵ at 360 nm. It is probable that the literature value experienced interference at 235 nm that was not present within these measurements.

Table 1 Molar absorptivity values ϵ ($\text{M}^{-1} \text{ cm}^{-1}$) of chlorine-containing species (Körtvélyesi 2004)

Chlorine-containing species	ϵ ($\text{M}^{-1} \text{ cm}^{-1}$)		
	235 nm	260 nm	360 nm
HOCl	90.6	37.7	0
ClO_2^-	69.2	148.2	2
ClO_2	128 ^a	55.9	1129

^aOwn experimental value

Baseline and slope corrections were applied to all the spectra obtained, and the absorbance contribution from other species was subtracted in order to obtain the concentration of the species of interest. All the experiments were done three times.

Iodometric titration

The iodometric titration was used to confirm the concentrations of HOCl, ClO_2^- , ClO_3^- and ClO_2 in the system. The method was first proposed by Wartiovaara (1982) and is based on the reduction of chlorine species by iodine ions at different pH values.

pKa measurement

A pH titration was used to identify the pKa of CEM-DABCO. An aqueous solution of CEM-DABCO (50 mM, 5 ml) with original pH 3.36 was acidified to pH 2.45 with a slow addition of 2.5 M HCl. Then, the sample was titrated with 1 M NaOH, monitoring the changes in pH.

Results and discussion

Optimal pH for the chloroammonium cation of CEM-DABCO

Chloroammonium cations are formed between HOCl and unprotonated tertiary amines (Prütz 1998), with the protonation of the catalyst reducing its ability to form the chloroammonium cation. To determine the pKa of CEM-DABCO, its acidic solution was titrated with NaOH (Fig. 3). The titration curve has two inflection points at pH 3.0 and 7.5, confirming the results from previous studies (Dawson

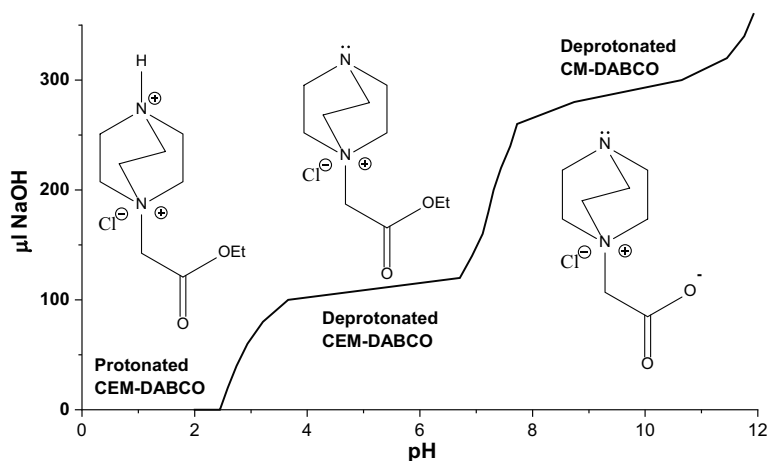


Fig. 3 Titration curve of CEM-DABCO

2018). The first value corresponds to the pKa of CEM-DABCO, while the second inflection was likely caused by the alkali-catalyzed hydrolysis of the methyl ester and neutralization of the formed CM-DABCO (Dawson 2018). On the other hand, HOCl is always in equilibrium with other chlorine species (Cl_2 and ClO^-). This equilibrium is pH dependent, with HOCl being the dominant chlorine species between pH 3.5–7.5. As a compromise, pH 5 was selected for the experiments. At this pH, the chloroammonium formation is fast due to the abundance of HOCl and unprotonated CEM-DABCO. This pH is similar to the range where the chloroammonium cation of the other alkyl-substituted DABCO was seen (Afsahi et al. 2019).

Catalyst stability

In buffer pH 5

The pH 5 buffer solution, DABCO and CEM-DABCO have their maximum absorbance in the same wavelength region, from 198 to 203 nm. The spectra of the buffer were subtracted to obtain the molar absorptivity values of the catalysts. DABCO and CEM-DABCO have molar absorptivities of $478 \text{ M}^{-1} \text{ cm}^{-1}$ (at 203 nm) and $317 \text{ M}^{-1} \text{ cm}^{-1}$ (at 201 nm) respectively.

DABCO and CEM-DABCO were stable in buffer pH 5, presenting no change in the absorbance value at 201 and 203 nm during a 600-s measurement. No decrease in the absorbance at 201–203 nm nor new peaks were detected. These results are consistent with general knowledge of amines stability in aqueous environment (McMurry 1998). In aqueous solutions, amines (such as DABCO and CEM-DABCO) reach equilibrium by receiving H^+ from water or the buffer. CEM-DABCO is additionally a quaternary ammonium salt, with a chloride counter ion, and thus, would dissociate in solution. The catalyst is therefore positively charged even before amine protonation. At pH 5, DABCO is similarly positively charged, but this is due to the protonation of one amine. No other changes were expected in CEM-DABCO at pH 5 since esters are stable at this pH (McMurry 1998) and catalyzed hydrolysis of CEM-DABCO is a slow process that would require a significantly longer time frame to take place.

With chlorite ions

The stability of DABCO and CEM-DABCO in ClO_2^- was analyzed by mixing equal moles of catalyst and ClO_2^- at pH 5. Figure 4 presents the spectra of ClO_2^- and the catalysts at 0.6, 300 and 600 s. Figure 4 a shows the spectra of ClO_2^- at pH 5. As expected (Shelly 1960) at this mildly acidic pH, ClO_2^- is consumed, shown by a decrease in the absorbance at 260 nm, and ClO_2 is produced, with an increase in the absorbance at 360 nm. A similar behavior is observed in Fig. 4 b, where CEM-DABCO is additionally present in the system, suggesting that CEM-DABCO is not reacting with ClO_2^- . The spectra of ClO_2^- with DABCO are presented in Fig. 4 c. At pH 5, ClO_2^- is converted into ClO_2 , which in turn reacts with DABCO. Hence, DABCO is not stable in the presence of ClO_2^- at pH 5.

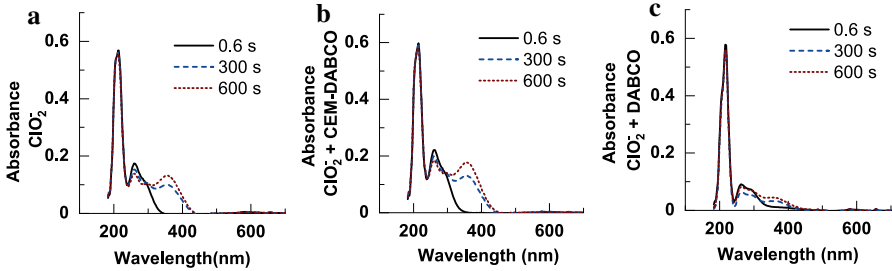


Fig. 4 UV/Vis spectra of ClO_2^- with tertiary amine catalysts at pH 5 (7.5 mM and 7.5 mM, respectively). **a** ClO_2^- , **b** ClO_2^- and CEM-DABCO, **c** ClO_2^- and DABCO

In hypochlorous acid

The stability of DABCO and CEM-DABCO with HOCl was studied by mixing equal moles of HOCl with the catalyst at pH 5. Figure 5a–c presents the spectra of HOCl in buffer with the catalysts. HOCl degrades slowly at pH 5 (Fig. 5a), which can be observed from the decrease in the absorbance at 235 nm in time. The addition of CEM-DABCO to HOCl (Fig. 5b) produces the chloroammonium cation, which in this case seems to have a similar absorption and stability to HOCl at pH 5. In contrast, DABCO reacts rapidly with HOCl (Fig. 5c), in the reaction described by Dennis et al. (1967), with the chloroammonium cation degrading to 1,4-dichloropiperazine and formaldehyde (Dennis et al. 1967). The very broad and intense peak of absorbance from 200 to 380 nm was also observed in similar experiments by Rosenblatt et al. (1972), who proposed that the peak is related to the chloroammonium cation and its degradation products, with a chloroammonium cation molar absorptivity value of $139 \text{ M}^{-1} \text{ cm}^{-1}$ at 357 nm.

These findings on the UV/Vis absorbance of CEM-DABCO and DABCO relate to previous studies, which have shown the poor predictability in the visibility of the chloroammonium cation. For example, the chloroquinuclidinium ion has shown a visible absorbance, while the trimethyleammonium ion has not (Ellis and Soper 1954; Pitman et al. 1969). A possible hypothesis is that the chloroammonium itself

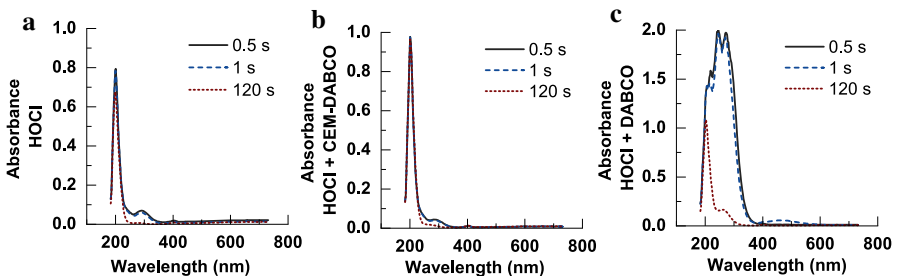


Fig. 5 UV/Vis spectra of HOCl with tertiary amine catalysts at pH 5 (5 mM and 5 mM, respectively). **a** HOCl, **b** HOCl and CEM-DABCO, **c** HOCl and DABCO

should have a similar absorbance to the catalyst, and that the visible new peaks correspond mostly to the degradation products of the chloroammonium cations.

Catalyst stability with chlorine dioxide

The stability of DABCO and CEM-DABCO in ClO_2 was analyzed by mixing equal moles of ClO_2 and catalysts in the buffer solution. Figure 6 presents the spectra of the mixed solutions at 0.26 s and after 600 s. It can be seen that at pH 5, ClO_2 is unstable (Körtvélyesi 2004), degrading over time, shown by a decrease in its absorbance at 360 nm. A similar decrease in the absorbance of ClO_2 is observed in Fig. 6b, meaning that CEM-DABCO does not contribute to ClO_2 degradation, and hence, is stable in the presence of ClO_2 . Figure 6c shows the spectra of DABCO and ClO_2 . As reported by previous studies (Dennis et al. 1967; Hull et al. 1967), ClO_2 degrades DABCO, which is observed in the decrease in the absorbance at 360 nm. The oxidation of DABCO by ClO_2 produces piperazine, formaldehyde and chlorite ions (Hull et al. 1967; Dennis et al. 1967) causing an increase in absorbance at 201 nm and at 260 nm. Figure 6d summarizes the rate of degradation of ClO_2 in time with each catalyst. Notably, there is a lower rate of degradation of ClO_2 in the presence of CEM-DABCO than in the reference system. This smaller rate suggests that the catalyst is both stable and has a positive effect on ClO_2 stability.

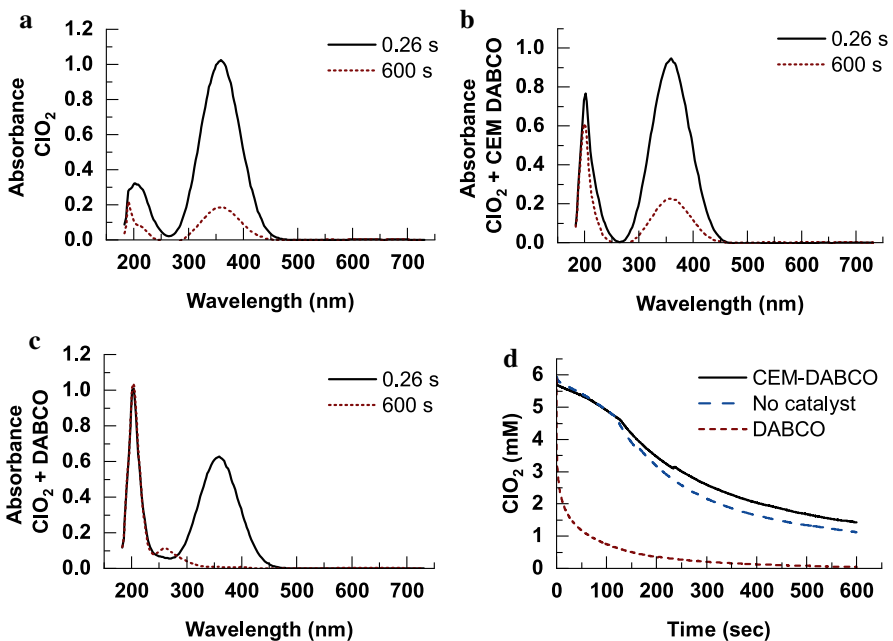


Fig. 6 UV/Vis spectra of ClO_2 with tertiary amine catalysts at pH 5 (6 mM and 5 mM respectively). **a** ClO_2 , **b** ClO_2 and CEM-DABCO, **c** ClO_2 and DABCO, **d** ClO_2 concentration calculated by absorbance at 360 nm

Effect of tertiary amine catalyst on the reaction of hypochlorous acid with chlorite ions

As discussed, the reaction between HOCl and ClO_2^- is a significant reaction in chlorine dioxide industrial treatments. It produces dichlorine dioxide (Cl_2O_2) as an intermediate species, and this then further reacts with other chlorine species and with water, regenerating ClO_2 , but also producing chlorate and chloride ions. Figure 7 presents the ClO_2 generation from the reaction of HOCl and ClO_2^- at pH 5. The catalyzed systems with DABCO and CEM-DABCO display a faster ClO_2 production than the non-catalyzed reaction. In less than one second (1 s), approximately 5 mM of ClO_2 are produced, while it takes more than twenty seconds (20 s) to produce the same amount in the non-catalyzed reaction. Using Fig. 7 a, it was also possible to calculate the initial speed of reaction (k) for ClO_2 formation. The initial rate of the non-catalyzed, DABCO-catalyzed, and CEM-DABCO-catalyzed reactions were 0.4, 20 and 30 mM s^{-1} , respectively. Hence, the ClO_2 formation of the CEM-DABCO-catalyzed reaction of HOCl with ClO_2^- is approximately 80 times faster than the non-catalyzed one.

The main difference between the two catalyzed systems is the stability of their catalysts. CEM-DABCO is stable, and hence, it can be assumed that the increase in the speed of chlorine dioxide formation is completely due to the catalyst. In contrast, DABCO is unstable in the presence of ClO_2 , forming formaldehyde as a degradation product, which has been reported to react with HClO_2 , regenerating ClO_2 (Ventorim et al. 2005; Jiang et al. 2007). Therefore, the catalytic effect in the DABCO system should be considered as the overall impact of both DABCO and formaldehyde.

The change in the reagent concentrations is presented in Fig. 7b and c, where the HOCl and ClO_2^- are consumed rapidly in the catalyzed reactions. In less than 1 s, the HOCl concentration drops from 5 to 2 mM in the CEM-DABCO-catalyzed reaction, while it takes approximately 15 s to reach the same concentration of HOCl in the non-catalyzed reaction. The 5 mM of ClO_2^- was fully consumed in less than 1 s when CEM-DABCO was used, whereas it took more than 20 s to consume the same amount of ClO_2^- in the non-catalyzed reaction. The apparent lower consumption of ClO_2^- (2.5 mM) and HOCl (0.5 mM) in the DABCO-catalyzed reaction should be

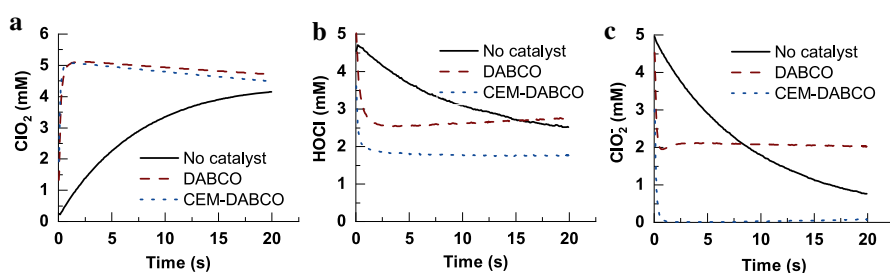
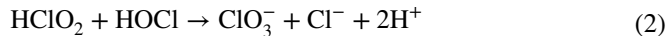
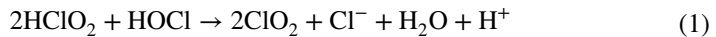


Fig. 7 ClO_2 production from the catalyzed and non-catalyzed reaction of HOCl with ClO_2^- at pH 5, initial concentrations of ClO_2 0 mM, HOCl 5 mM, ClO_2^- 5 mM and catalysts 0.5 mM. **a** ClO_2 amounts calculated from the absorbance at 359 nm, **b** HOCl concentration, measured absorbance at 234 nm, **c** ClO_2^- concentration, measured absorbance at 260 nm

interpreted as degradation products from the chloroammonium cation of DABCO which are formed in this range of wavelengths. These results support that the tertiary amines increase the speed of reaction of chlorine dioxide regeneration and suggest that the stoichiometry of the system remains unchanged.

An iodometric titration was used to confirm the hypothesis that the catalyst does not change the stoichiometry of the reaction of HOCl with ClO_2^- . This technique was used to overcome the spectrometry restrictions on identifying chlorate (ClO_3^-), and the uncertainty of concentrations in a mix of chlorinated species in the absorbance at 235 and 260 nm. Table 2 presents the final amounts of ClO_2 , HOCl, and ClO_3^- (at 15 and 60 s) in the reaction system of HOCl, ClO_2^- and catalyst. In general, it can be observed that similar amounts of ClO_2 , HOCl and ClO_3^- are produced with or without either catalyst. These results support the hypothesis that the equilibria of the reaction are not changed by addition of catalyst.

Based on these titration results and previous knowledge of the stoichiometry and reaction rates of the reaction of HOCl with ClO_2^- , as shown in Fig. 1 (Tarvo et al. 2009; Jia et al. 2000), a rudimentary overall balance of Cl is estimated. The initial concentration of Cl atoms in the mixture was 14.3 ± 1.0 mM (6 mM HOCl, 5.2 mM ClO_2^- and 3.1 mM ClO_3^-), and after 15 s there remains only an average of 10.9 mM of Cl atoms (4.7 mM ClO_2 , 2.4 mM HOCl and 3.8 mM ClO_3^-). Henceforth, it is evident that approximately 3.4 mM Cl atoms are missing.



Analyzing Fig. 1, the reagents (HOCl and ClO_2^-) react in the rate determining step forming the intermediate Cl_2O_2 , and afterward, there are four possible routes for it to react (Reactions 2, 3, 4 and 5). In this stoichiometry determining part of the reaction, Reaction 4 is known to be predominant over Reaction 3 in the production of ClO_2 (Tarvo et al. 2009; Jia et al. 2000; Fabian and Gordon 1992). Combining Reactions 1 and 4 (Eq. 1), and knowing that the average initial amounts of HClO_2 and HOCl in the system was 5 mM, it can be supported that approximately 4.7 mM of ClO_2 and 2.35 mM of Cl^- are produced when the equilibrium is reached, at

Table 2 Results of iodometric titration of chlorinated species of the system

Chlorine-containing species (\pm mM)	Concentration (mM)					
	15 s			60 s		
	No catalyst	DABCO	CEM-DABCO	No catalyst	DABCO	CEM-DABCO
ClO_2 (± 0.2)	4.7	4.7	4.6	4.0	4.7	4.5
HOCl (± 0.6)	2.0	2.6	2.4	1.5	0.1	0.6
ClO_3^- (± 0.3)	3.7	3.8	3.9	3.8	4.0	3.9

Initial concentrations of 6 mM HOCl, 5.2 mM ClO_2^- , 3.1 mM ClO_3^- , 0 mM ClO_2 and 0.05 mM of catalyst in buffer pH 5

approximately 15 s. A similar assumption can be made for the production of ClO_3^- , which can be produced either via Reactions 2 and 5, with Reaction 2 being faster than Reaction 5 (Jia et al. 2000; Fabian and Gordon 1992). Therefore, combining Reactions 1 and 2 (Eq. 2), and knowing that 0.7 mMol of ClO_3^- was produced, it can be assumed that a similar amount of Cl^- was generated via Reaction 2. In summary, at least 3.2 mMol of Cl^- is produced in the system after 15 s. A different situation results after 60 s, where chlorine dioxide is degraded due to the pH and an even more complex reaction system is taking place and as such will not be discussed in this article.

Impact of catalyst dosage

As shown, due to its high stability and activity in the reaction system, CEM-DABCO has a high potential as a catalyst, and hence, it is interesting to analyze the effect of its chloroammonium cation in the production of chlorine dioxide. Figure 8 presents the impact of catalyst dosage on the production of ClO_2 . It can be seen that while higher amounts of catalyst result in higher k values, they eventually lead to similar chlorine dioxide amounts (5.2 mM ClO_2), displaying that the stoichiometry of the reaction is not changed by the catalyst, taking into consideration that this technique has an error of $\pm 5\%$.

The initial rate of reaction of the non-catalyzed ClO_2 regeneration is doubled with 0.005 mM of CEM-DABCO and increases with the catalyst amount up to 27.2 mM/s (with 0.5 mM of catalyst), which corresponds to an increase of 45 times the original speed of reaction. The small differences among the k values presented in the current and previous sections are believed to originate from the small differences in the amounts of initial reagents (HOCl and ClO_2^-) as well as some impurities present in them, especially NaClO_3 or NaCl (Tarvo 2010).

Table 3 presents the results of the titration that confirm the hypothesis that the stoichiometry of the reaction is not modified by higher amounts of catalyst. At 15 s, the amounts of ClO_2 and ClO_2^- are similar, but after 60 s, the titration reveals a

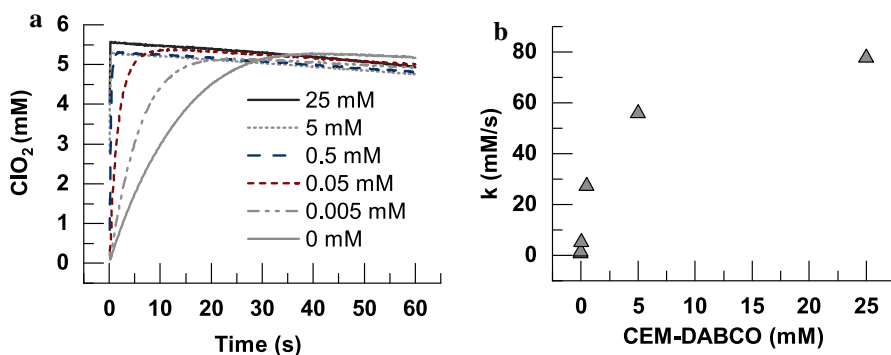


Fig. 8 Effect of catalyst dosage on the production of ClO_2 from the reaction of HOCl with ClO_2^- (both reagents 5 mM). **a** ClO_2 production as a function of time, **b** rate of ClO_2 production as a function of catalyst concentration

Table 3 Results of iodometric titration of the reaction of ClO_2^- ions with HOCl at different CEM-DABCO dosages

Chlorine-containing species (\pm mM)	Concentration (mM)							
	15 s				60 s			
	CEM-DABCO							
	25 mM	5 mM	0.05 mM	0 mM	25 mM	5 mM	0.05 mM	0 mM
ClO_2 (± 0.2)	4.9	4.8	4.6	4.7	4.4	4.5	4.5	4.0
HOCl (± 0.6)	2.0	2.1	2.4	2.0	–	–	0.6	1.5
ClO_3^- (± 0.3)	3.6	3.6	3.9	3.7	3.8	3.6	3.9	3.8

Initial concentrations of 6 mM HOCl, 5.2 mM ClO_2^- and 3.1 mM ClO_3^- in buffer pH 5

slightly higher amount of ClO_2 for the catalyzed reactions, suggesting that the catalyst has a positive impact on the stability of ClO_2 .

Conclusion

CEM-DABCO catalyzes successfully the reaction of HOCl with ClO_2^- . When this tertiary amine catalyst is present in the reaction system, the rate of ClO_2 production is increased, and the ClO_2 is of a higher stability. The catalyst dosage has a significant impact on the initial rate of formation of ClO_2 , but even small dosages (such as 0.001 times the amounts of reagents) can still double the initial speed of reaction. Higher catalyst amounts lead to faster production of ClO_2 , up to 8, 40 or even more than 90 times faster, than the non-catalyzed reaction. The positive effect of the catalyst on ClO_2 amounts can be explained by its high stability with ClO_2 and ClO_2^- , unlike its base structure DABCO, which degrades rapidly in their presence.

This study constitutes an advance in the knowledge of chlorine chemistry and presents potential applications in the production of ClO_2 , or within applications where it is consumed via the oxidation of organic substrates.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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