Intracluster Sulphur Dioxide Oxidation by Sodium Chlorite Anions: A Mass Spectrometric Study

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Abstract: The reactivity of [NaLClO x ] − cluster anions (L = ClO x − ; x = 0–3) with sulphur dioxide has been investigated in the gas phase by ion–molecule reaction experiments (IMR) performed in an in-house modified Ion Trap mass spectrometer (IT-MS). The kinetic analysis revealed that SO 2 is efficiently oxidised by oxygen-atom (OAT), oxygen-ion (OIT) and double oxygen transfer (DOT) reactions. The main difference from the previously investigated free reactive ClO x − is the occurrence of intracluster OIT and DOT processes, which are mediated by the different ligands of the chlorite anion. This gas-phase study highlights the importance of studying the intrinsic properties of simple reacting species, with the aim of elucidating the elementary steps of complex processes occurring in solution, such as the oxidation of sulphur dioxide.

Keywords: cluster reactivity; sulphur dioxide; sodium chlorite; mass spectrometry; ion-molecule reactions; oxidation reactions

1. Introduction

Pollution and other environmental issues are typically associated with the atmospheric emissions of exhaust flue gases produced by power plants and industries [1]. Different technologies, collectively known as flue gas cleaning processes, attempt to mitigate the release of greenhouse gases deriving from the burning of coal to generate electrical power [2]. Most efforts in this field are aimed at planning pollutant-control strategies to reduce sulphur dioxide which is referred to as the main precursor of acid rainfalls and atmospheric particulate [3–5]. To this end, the European Union established the 2016/2284/UE Regulation that intends to progressively reduce SO 2 emissions until 2029 and for the next few years [6]. Among the flue gas desulphurization (FGD) methods, the wet scrubbing system is a low-cost and simple technology based on the reaction between SO 2 and an alkaline sorbent, typically limestone [7–9]. Although engineers mostly design separate air-cleaning devices for individual gas emission removal, the search for multi-pollutant control systems would reduce the need for large installation areas and operation costs [10]. To this end, sodium chlorite (NaClO 2 ) is one of the most effective reagents for the simultaneous removal of oxides of sulphur (SO x ) and nitrogen (NO x ) [11]. The addition of this compound to seawater solution has been recently exploited to improve the elimination of SO 2 and favour the development of environmentally friendly seawater-based FGD [12].

The strong oxidative properties of NaClO 2 allows the conversion of sulphites (SO 3 2− ) produced by SO 2 absorption to the harmless sulphates (SO 4 2− ) that are easily solubilized in water and thus removed [13,14]. Nevertheless, many factors can affect the outcome of the scrubbing process (e.g., pH, temperature, oxidant concentration, oxidant/gas contact time, volumetric gas, liquid flow rates) and the influence of these parameters has to be carefully evaluated in the design of the operating systems [15–17]. For instance, solution salinity is known to increase SO 2 absorption efficiency, and under alkaline conditions needed for SO 2/SO 3 2− conversion, the occurrence of a gas-solid interface reaction between SO 2 and NaClO 2 gives rise to the formation of Cl − , ClO − and OClO − chlorinated species which may
enhance the concomitant NO oxidation in multi-pollutant removal plants [18,19]. On the other side, the above-mentioned factors can contribute to masking the intrinsic reactivity of NaClO₂ towards sulphur dioxide preventing the elucidation of the mechanistic details that lead to the oxidation of SO₂ and the formation of collateral products.

A successful strategy to avoid solution interfering effects and investigate the chemical processes at a strictly molecular level consists in performing gas-phase studies by mass spectrometry [20–26]. This technique is one of the most routinely employed for analytical purposes in a plethora of research fields spanning, inter alia, from foods and drugs to biology [27–34] or from geology to atmospheric chemistry [35–39]. Less well known is the use of mass spectrometry in fields such as catalysis, nevertheless, in the last years, mass spectrometry has been widely employed to assess the elementary steps of a chemical transformation by unravelling mechanistic pathways and elucidating the factors which affect the reaction outcome [40–46]. Accordingly, ion-molecule reaction (IMR) experiments were largely intended to investigate the reactivity of ionic reagents generated at their ground state towards neutral species under single-collision conditions. The gas-phase reaction of free ClO⁻ and ClO₂⁻ anions towards SO₂ has actually provided important information on the intrinsic properties of naked chloride leading to the oxidation of sulphur dioxide to SO₃, SO₃⁻ and SO₄⁻, with the concomitant formation of the chlorinated species ClO⁻, ClO₂⁻, and Cl⁻ [47]. These reaction channels, respectively referred to as oxygen-atom (OAT), oxygen-ion (OIT), and double oxygen transfer (DOT), may represent simplified models of large-scale reactions occurring in the atmosphere or involved in the flue-gas desulphurization processes.

In addition, electrospray ionization mass spectrometry has been long-time devoted to the study of salt speciation [48–50] showing its capability in controlling the size and charge of cluster ions. As a result, ionic clusters can be considered miniaturized systems to investigate the intrinsic features of matter aggregation phenomena [51,52]. Accordingly, the study of the gas-phase reactions of SO₂ with positive and negative carbonate cluster ions contributed to highlighting the major role of the charge in the kinetics of smallest clusters, as well as the different reactivity when charged cluster are ligated to a NaOH molecule [53]. Indeed, a point-charge ligand can generate oriented external electric fields able to change thermodynamics and kinetics of a gas-phase thermal process by controlling the reaction mechanism, efficiencies, and product distribution [54–56].

Continuing with our studies focused on the chemistry of sulphur dioxide [57–62], here we report on the gas-phase reactivity of negatively charged chloride cluster ions, [Na₃ClO₂](L = ClO⁻ with x = 0–3), towards SO₂ investigated by ion-molecule reaction experiments. In this way, the effect of the ligation of a neutral molecule to ClO₂⁻ that changes the ion size and charge distribution of the cluster has been evaluated based on the known reactivity of naked ClO₂⁻ species with SO₂.

2. Results and Discussion

Oxo-halogenated ions investigated in this work were generated by the negative electrospray ionization of NaClO₂ solutions typically yielding a series of singly-charged cluster ions in which NaClO₂ is clustered to the ClO₂⁻ anion to form aggregates resembling the general formula [(NaClO₂)ₙClO₂⁻], n varying from 1 to 4 in the m/z range 100–500 (Figure S1). Aggregation phenomena are indeed characteristic of electrosprayed saline compounds [49] and are influenced by the solute concentrations and source parameters [53]. Furthermore, the electric field applied between the capillary and the skimmer plate accounts for the occurrence of electrochemical reactions at the conductive contact-solution interface near the ES emitter [63]. The detection of ClO⁻ x (x = 0, 1, 3) anions in addition to the ClO₂⁻ parent species suggests the effective occurrence of in-source redox processes. For x = 1 and 3, the corresponding ClO⁻ and ClO₃⁻ anions do not undergo significant aggregation phenomena. On the contrary, Cl⁻ anions promote aggregation with NaClO₂ to form [(NaClO₂)ₙCl⁻]⁻ ions (n = 1–5), and mixed clusters of general formula [Na₃ClₓO₂y]⁻ were also identified as minor species, as shown in the Supplementary Materials (Figure S1).
The simplest ClO$_2^-$ clusters for $n = 1$ were found at $m/z$ 125 and 157 and respectively attributed to the $^{35}$chlorine isotopologue of [NaCl-ClO$_2$]$^-$ and [NaClO$_2$-ClO$_2$]$^-$ species. The assignment was based on the distinctive $^{35/37}$Cl isotope pattern and on the corresponding collision-induced dissociation (CID) mass spectra. The ion [Na$^{35}$Cl.$^{35}$ClO$_2$]$^-$ at $m/z$ 125 predominantly fragments by losing a Na$^{35}$Cl neutral counterpart giving rise to the $^{35}$ClO$_2^-$ daughter ion at $m/z$ 67 (Figure 1a). The gas-phase decomposition of the corresponding $^{35/37}$Cl isotopomer ($m/z$ 127) predictably leads to the formation of an equal ratio of $^{35}$ClO$_2^-$ and $^{37}$ClO$_2^-$ fragments at $m/z$ 67 and 69, respectively (Figure 1b). The parent ion can be therefore described as a complex of the type [Cl-Na-ClO$_2$]$^-$ in which both the chloride (Cl$^-$) and chlorite (ClO$_2^-$) anions are coordinated to the sodium cation (Na$^+$). In particular, the chlorite moiety is reasonably consistent with an OCIO$^-$ species rather than with the more stable ClOO$^-$ isomer, the presence of which can be excluded considering the structure of the precursor salt, NaClO$_2$, and the high energy barrier to the isomerization, calculated to be 51.1 kcal mol$^{-1}$, [47] which cannot be overcome by the ions during the ionization process.

![ESI(-) CID mass spectra of the isolated (a) [Na$^{35}$Cl.$^{35}$ClO$_2$]$^-$ at $m/z$ 125 and (b) [Na$^{35}$Cl.$^{37}$ClO$_2$]$^-$ and [Na$^{37}$Cl.$^{35}$ClO$_2$]$^-$ at $m/z$ 127.](image)

Similarly, the CID mass spectrum of the ionic species [Na$^{35}$ClO$_2$.$^{35}$ClO$_2$]$^-$ at $m/z$ 157 shows the only daughter ion $^{35}$ClO$_2^-$ at $m/z$ 67, arising from the loss of a NaClO$_2$ neutral counterpart (Figure 2a). Accordingly, the gas-phase decomposition of the isotopomer at $m/z$ 159 leads to the formation of an equal ratio of $^{35}$ClO$_2^-$ and $^{37}$ClO$_2^-$ fragment ions at $m/z$ 67 and 69 (Figure 2b), accounting for the symmetrical complex [ClO$_2$-Na-ClO$_2$]$^-$.
A kinetic plot showing the time progress of the reaction is displayed in Figure 3. The identity of the cluster and are not released as free species. Accordingly, the whole mechanistic pathways, measuring the rate constants for each reaction channel, and structurally characterizing the ionic products by CID experiments.

2.1. Reactivity of [Cl-Na-ClO₂]⁻ Cluster Anion

[Cl-Na-ClO₂]⁻ cluster anions react with SO₂ at room temperature giving rise to the products shown in Scheme 1, through a complex series of parallel and consecutive reactions. A kinetic plot showing the time progress of the reaction is displayed in Figure 3. The identity of the ionic products from reactions 1–5 has been probed by collision-induced dissociation as discussed in the following. As reported in Table 1, the reaction of [Cl-Na-ClO₂]⁻ has a rate constant (k_{dec}) of 2.88 × 10^{-10} (±30%) cm³ s⁻¹ mol⁻¹ and an efficiency (k/k_{coll}) of 24.2%.
Scheme 1. Reactivity scheme $[\text{Cl-Na-ClO}_2]^{-}$ ions ($m/z = 125$) with SO$_2$. Oxygen transfer channels (OIT, OAT, DOT) and bimolecular rate constants are indicated for each reaction.

Figure 3. Kinetic plot and best fit lines of the reaction of isolated $[\text{NaCl-ClO}_2]^{-}$ ions ($m/z = 125$) with SO$_2$. P SO$_2$ = $5.26 \times 10^{-7}$ Torr. ■ $[\text{Cl-Na-ClO}_2]^{-}$ ($m/z = 125$) ($R^2 = 0.9991$); ● $[\text{Cl-Na-SO}_3]^{-}$ ($m/z = 138$) ($R^2 = 0.9986$); ○ $[\text{Cl-Na-ClO}]^{-}$ ($m/z = 109$) ($R^2 = 0.9770$); ◊ $[\text{Cl-Na-SO}_4]^{-}$ ($m/z = 154$) ($R^2 = 0.9915$); × $[\text{Cl-SO}_3]^{-}$ ($m/z = 131$) ($R^2 = 0.9868$); ◐ $[\text{SO}_4]^{-}$ ($m/z = 96$) ($R^2 = 0.9846$); △ $[\text{Cl-Na-Cl}]^{-}$ ($m/z = 93$) ($R^2 = 0.9946$); ○ $[\text{Cl-SO}_3]^{-}$ ($m/z = 115$) ($R^2 = 0.9946$).

Although the larger size of $[\text{Cl-Na-ClO}_2]^{-}$ is predictably responsible for the decrease of the overall reaction rate compared to that of naked ClO$_2^{-}$ ($2.88$ vs. $9.10 \times 10^{-10}$ cm$^3$ s$^{-1}$ mol$^{-1}$), the intrinsic reactivity of the two ionic species is comparable, except for small differences in the branching ratios of the three oxygen transfer reactions. For the sake of clarity, the reactivity, OIT, OAT and DOT, is indicated in each reaction channel.
which a Cl$^{−}$ (2.1)

The rate constants of the two competitive processes are respectively $k_1$ and $k_2$. The interaction of the Cl$^{−}$ anion with SO$_2$ plays a spectator role, whereas the sodium cation is reasonably involved in the coordination of both Cl$^{−}$ and SO$_3^{−}$ anions.

Further, [Cl−Na−SO$_3^{−}$] was found to be unreactive towards SO$_2$ thus confirming the presence of the two notoriously inert Cl$^{−}$ and SO$_3^{−}$ moieties [47]. The Cl$^{−}$ anion only plays a spectator role, whereas the sodium cation is reasonably involved in the coordination of both Cl$^{−}$ and SO$_3^{−}$ anions.

A minor channel gives rise to [Cl−Na−ClO$_3^{−}$] at $m/z$ 109 and SO$_3$ in Equation (2), with a rate constant $k_3$ of $2.51 \times 10^{−11}$ (±30%) cm$^3$ s$^{−1}$ mol$^{−1}$ (Table 2), and a branching ratio of 8.8% (Table 1). The product ion [Cl−Na−ClO$_3^{−}$] at $m/z$ 109 resembles an aggregate in which a Cl$^{−}$ spectator anion and a ClO$^{−}$ moiety are both coordinated to sodium cation, as evidenced by its CID mass spectrum. Through this path, SO$_2$ is therefore oxidised to SO$_3$ by an oxygen atom transfer (OAT) reaction. Once formed, [Cl−Na−ClO$_3^{−}$] displays the distinctive reactivity of the surrounding ClO$^{−}$ moiety towards SO$_2$ that consists in a further SO$_2$ to SO$_3$ conversion (Equation (2.1)), through a second OAT process, and in an intracluster reaction giving [Cl−SO$_3^{−}$] at $m/z$ 115 through an OIT process (Equation (2.2)).

The rate constants of the two competitive processes are respectively $k_{21} = 7.53 \times 10^{−10}$ (±30%) and $k_{22} = 7.43 \times 10^{−11}$ (±30%) cm$^3$ s$^{−1}$ mol$^{−1}$ (Table 2). Not surprisingly, the OAT undergone by [Cl−Na−ClO$_3^{−}$] (Equation (2)) is slower with respect to the same process undergone by [Cl−Na−ClO$_3^{−}$] (Equation (2.1)), reflecting the different reactivity of the free

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**Table 1.** Rate constants (cm$^3$ s$^{−1}$ mol$^{−1}$), branching ratios (%Σ) and efficiencies ($k/k_{coll}$) for the reactions of [L−M−ClO$_3^{−}$] ($L = Cl, F, Br, I, ClO$_2$, SO$_3$; M = Na, Li] anions with SO$_2$. The reaction of ClO$_3^{−}$ with SO$_2$ is also reported for comparative purposes. OIT: oxygen ion transfer; OAT: oxygen atom transfer; DOT: double oxygen transfer.

| Reaction | $k_{dec} \times 10^{−10}$ | $k_{coll}$ (%) | OIT | OAT | DOT |
|----------|---------------------------|----------------|------|-----|-----|
| ClO$_3^{−}$ + SO$_2$ [47] | 9.10 | 63.8 | 86.5 | 4.2 | 9.3 |
| [Cl−Na−ClO$_3^{−}$] + SO$_2$ | 2.88 | 24.2 | 74.2 | 8.8 | 17.0 |
| [F−Na−ClO$_2^{−}$] + SO$_2$ | 3.75 | 30.8 | 89.2 | 3.7 | 7.1 |
| [Br−Na−ClO$_2^{−}$] + SO$_2$ | 2.12 | 18.7 | 73.4 | 10.1 | 16.5 |
| [I−Na−ClO$_2^{−}$] + SO$_2$ | 1.85 | 16.8 | 68.9 | 13.7 | 17.4 |
| [Cl−Li−ClO$_2^{−}$] + SO$_2$ | 1.81 | 14.5 | 84.7 | 7.7 | 7.4 |
| [ClO$_2^{−}$−Na−ClO$_2^{−}$] + SO$_2$ | 7.48 | 66.0 | 81.8 | 4.8 | 13.4 |
| [SO$_3^{−}$−Na−ClO$_2^{−}$] + SO$_2$ | 3.74 | 33.0 | 70.4 | 6.9 | 22.7 |
| [(NaClO$_2$)$_2$−ClO$_2^{−}$] + SO$_2$ | 7.39 | 68.1 | - | - | - |

$\S$ ±30%.

Furthermore, [Cl−Na−SO$_3^{−}$] was found to be unreactive towards SO$_2$ thus confirming the presence of the two notoriously inert Cl$^{−}$ and SO$_3^{−}$ moieties [47]. The Cl$^{−}$ anion only plays a spectator role, whereas the sodium cation is reasonably involved in the coordination of both Cl$^{−}$ and SO$_3^{−}$ anions.

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**Table 2.** Rate constants (cm$^3$ mol$^{−1}$ s$^{−1}$) for the reactions of the [Cl−Na−ClO$_2^{−}$] anion with SO$_2$. OIT: oxygen ion transfer; OAT: oxygen atom transfer; DOT: double oxygen transfer.

| Reactivity | $k \times 10^{−10}$ cm$^3$ mol$^{−1}$ s$^{−1}$ | $k_1$ | $k_2$ | $k_3$ | $k_4$ | $k_5$ |
|------------|-----------------------------------------------|------|------|------|------|------|
| OIT        |                                              | 2.13 | 0.743| 0.251| 0.147| 0.034|
| OAT        |                                              |      |      |      |      |      |
| DOT        |                                              |      |      |      |      |      |

$\S$ ±30%.
ClO$_2^-$ and ClO$^-$ species [47]. The first preferably oxidises SO$_2$ through an OIT process, whereas the OAT is faster in the case of ClO$^-$. Finally, the [Cl-Na-ClO$_2$]$^-$ parent ion is involved in different reactions collectively responsible for a double oxygen transfer (DOT) to SO$_2$ with the formation of product ions containing a sulphate anion, SO$_4^{2-}$ (Equations (3)–(5)). The sulphate moiety can be either found as a clustered ion, as in Equations (3) and (4), or it can be a free anion as in Equation (5). In Reactions (3) and (4), upon the oxidation of SO$_2$ to SO$_4^{2-}$, a NaCl or Cl$^-$ neutral moieties are respectively released. In any case, it is formed through an overall O$_2^-$ transfer and the DOT processes account for a branching ratio of 17.0% (Table 1).

The ionic product at m/z 154 (Equation (3)) is consistent with a [Cl-Na-SO$_4$]$^-$ structure according to its fragmentation into SO$_4^{2-}$ ion at m/z = 96 (Figure S4) and loss of the neutral NaCl. The reaction occurs with a rate constant k$_3$ of $3.06 \times 10^{-11}$ (±30%) cm$^3$ s$^{-1}$ mol$^{-1}$ and represents the main DOT path. Alternatively, the SO$_4^{2-}$ moiety can remain attached to the Cl$^-$ radical, and releasing a NaCl moiety leads to the product ion [Cl-SO$_4$]$^-$ at m/z 131 with a k$_4$ of $1.47 \times 10^{-11}$ (±30%) cm$^3$ s$^{-1}$ mol$^{-1}$ (Equation (4)). According to the electron affinity values for SO$_4$ (EA = 5.10 eV) and Cl (EA = 3.61 eV) [64], the negative charge of the [Cl-SO$_4$]$^-$ product ion is mostly located on the SO$_4$ moiety, as confirmed by the dissociation of this cluster into SO$_4^{2-}$ ion at m/z = 96 (Figure S5).

Finally, SO$_4^{2-}$ is also generated as a free ion through reaction 5 with a k$_5$ of $3.4 \times 10^{-12}$ (±30%) cm$^3$ s$^{-1}$ mol$^{-1}$. Not surprisingly, the free SO$_4^{2-}$ ion is the least abundant product formed through the DOT paths. In the clustered species, [Cl-SO$_4$]$^-$ and [Cl-Na-SO$_4$]$^-$, the negative charge can be more favourably dispersed in larger species.

The comparison with the reactivity of the free ClO$_2^-$ anion shows that also with the [Cl-Na-ClO$_2$]$^-$ clustered anions the OIT remains the main reaction channel. When ClO$_2^-$ was reacted with SO$_2$ the small differences in the electron affinities between ClO$^-$ (EA = 2.27 eV) and SO$_3$ (EA of 2.06 eV) [64] only resulted in close energies (−24.6 and −25.6 kcal mol$^{-1}$) calculated for the two alternative exit channels, namely SO$_3^{2-}$ (+ClO$^-$) and SO$_3$ (+ClO$^-$) [47]; therefore, the prevalence of the OIT process was attributed to kinetic factors. Contrarywise, thermochemical factors favoured the OAT reaction over the OIT process in the reactivity of the free ClO$^-$ anion with SO$_2$ due to the significantly higher electron affinity of Cl (EA = 3.61 eV) with respect to that of SO$_3$ (EA = 2.06 eV). Accordingly, in the reactivity of [Cl-Na-ClO$^-$] ion, OAT (Equation (2.1)) prevails over the OIT process (Equation (2.2)) by a ratio of ca. 10/1. The in-depth theoretical analyses performed on the free ClO$_2^-$ species [47] can also give some insights into the reactivity observed with the clustered chlorite anions. The potential energy surface (PES) of [OCIO-SO$_2$]$^-$ system, was characterised by an early transition state that accounts for the almost barrierless formation of SO$_3^{2-}$. In the TS, the negative charge is exclusively located on the preformed SO$_3$ group (1.02 e$^{-}$), that is prone to rapid dissociation into the sulphite radical anion, and that strongly competes with the OAT and DOT processes. The formation of SO$_3$ and SO$_4^{2-}$ occurs through common intermediates, found on the double well PES, which dissociate reflecting the endothermicity of the two processes. This theoretical analysis is well suited to also explain the reactivity observed for the ligated [Cl-Na-ClO$_2$]$^-$ cluster ions with SO$_2$, that is of the other ligated species described in the following sections. The NaCl ligand does not affect the outcome of the oxidation reactions. Rather, it seems to have the effect of spreading the charge on the cluster, eventually lowering the reaction rate.

Overall, an increase of DOT and OAT processes at the expense of OIT channel is evidenced for the [Cl-Na-ClO$_2$]$^-$ cluster ion with respect to the non-clustered ClO$_2^-$ anion.

Effect of the Ligand

To deeply investigate the role of the NaCl ligand in the reactivity of [Cl-Na-ClO$_2$]$^-$ ion towards SO$_2$, Cl$^-$ was first replaced by X anion (X = F, Br, I) to form the corresponding [X-Na-ClO$_2$]$^-$ reactive species and subsequently Li$^+$ was inserted in place of Na$^+$ to evaluate the role of the cation. Only non-redox-active ligands were used in order to make a
comparison with the effect of salinity in solution, where it is known that the increase in ionic strength determines an increase in the absorption efficiency of SO$_2$ [18].

As reported in Table 1, the overall rate constant ($k_{dec}$) increases with the charge density of X anion, reaching the highest value of $3.75 \times 10^{-10}$ ($\pm$30%) cm$^3$ s$^{-1}$ mol$^{-1}$ with the smallest F anion (ion radius = 136 pm) and the lowest value of $1.85 \times 10^{-10}$ ($\pm$30%) cm$^3$ s$^{-1}$ mol$^{-1}$ with the largest I anion (ion radius = 216 pm) (Table 1) [65].

Regarding the branching ratios of the three reaction channels, [I-Na-ClO$_2$]$^-$ and [Br-Na-ClO$_2$]$^-$ show a reactivity distribution comparable to that of the [Cl-Na-ClO$_2$]$^-$ ion. On the contrary, an increase of the OIT process at the expense of the OAT and DOT channels was reported for [F-Na-ClO$_2$]$^-$ cluster species. As a consequence of the high charge density on the fluoride ion, the [F-Na-SO$_3$]$^-$ product arising from the OIT process adds an SO$_2$ molecule giving rise to a labile adduct of the type [F-Na-SO$_3$-SO$_2$]$^-$ never observed with the other reactant ions. The OAT process increases down the halogen series, whereas the opposite occurs with the OIT process.

Passing to the cation effect, an opposite trend was observed, as the reaction rate decreases by increasing the positive charge density on the metal. The overall rate constant for the [Cl-Li-ClO$_2$]$^-$ + SO$_2$ reaction is indeed almost three times lower than the corresponding value for the [Cl-Na-ClO$_2$]$^-$ + SO$_2$ system, highlighting the central role of an external electric field in modelling the reaction kinetics. [54–56] Minor effect of the charge density is instead reported for the general reactivity scheme of [Cl-Li-ClO$_2$]$^-$ anion.

The main role played by the different ligands described above might be due to the spreading the negative charge of ClO$_2^-$ within the cluster, the effect of which is reflected in the oxidative capacity of ClO$_2^-$ ion: the higher the charge density of the ligand, the faster the reaction. Passing from F$^-$ to I$^-$, the former forms a tighter ion pair with Na$^+$, making the chlorite anion more available to oxidise sulphur dioxide. A second effect concerns the steric hindrance to the approach of SO$_2$ due to the neutral ligand, whereby ligands of larger dimensions lead to a decrease in the overall reaction rate. An opposite effect is observed with the lithium cation, whose small size increases the interactions with both Cl$^-$ and ClO$_2^-$, reducing the oxygen transfer rate of the latter. The effect of the non-redox ligands here tested is different to that played in solution, where an increase in ionic strength (i.e., the salinity) has the effect of increasing the SO$_2$ absorption efficiency by the solutions and therefore the overall efficiency of wet scrubbing processes [18].

2.2. Reactivity of [ClO$_2$-Na-ClO$_2$]$^-$. Cluster Anion

Passing to [ClO$_2$-Na-ClO$_2$]$^-$ cluster ion, the reactive channels reported in Scheme 2 have been observed from the reaction with SO$_2$. The identity of the ionic products from Reactions (6)–(11) have been probed by collision–induced dissociation experiments as discussed below.

The reaction of [ClO$_2$-Na-ClO$_2$]$^-$ with SO$_2$ at 298 K is fast and efficient showing an overall rate constant ($k_{dec}$) of $7.48 \times 10^{-10}$ ($\pm$30%) cm$^3$ s$^{-1}$ mol$^{-1}$ at 298 K. This value is only 0.82 times lower than the corresponding one for the bare ClO$_2^-$ species, whereas the efficiencies ($k/k_{coll}$) of the two processes are similar (66.0% vs. 63.8%, Table 1). The intrinsic reactivity of the [ClO$_2$-Na-ClO$_2$]$^-$ anion towards SO$_2$ is comparable to that of the [Cl-Na-ClO$_2$]$^-$ species, as demonstrated by rather close branching ratios for the three reaction pathways (Table 1). Nonetheless, the concomitant presence of two reactive ClO$_2^-$ moieties in the [ClO$_2$-Na-ClO$_2$]$^-$ ion gives rise to an intricate reaction picture as shown in the above Scheme 2 and in the kinetic plot of Figure 4.
Scheme 2. Reactivity scheme [ClO₂⁻Na₂ClO₂]⁻ ions (m/z = 157) with SO₂. Oxygen transfer channels (OIT, OAT, DOT) and bimolecular rate constants are indicated for each reaction.

Figure 4. Kinetic plot and best fit lines of the reaction of isolated [NaClO₂−ClO₂]⁻ ions (m/z = 157) with SO₂. P SO₂ = 3.30 × 10⁻⁷ Torr. ■ [ClO₂⁻Na₂ClO₂]⁻ (m/z = 157) (R² = 0.9991); ▲ [ClO₂⁻Na₂SO₃]⁻ (m/z = 170) (R² = 0.9986); ● [SO₃⁻Na₂SO₃]⁻ (m/z = 183) (R² = 0.9998); × [ClO₂⁻Na₂ClO]⁻ (m/z = 141) (R² = 0.9888); ◊ [Cl⁻Na₂ClO₂]⁻ (m/z = 125) (R² = 0.9965); ● [Cl⁻Na₂SO₃]⁻ (m/z = 138) (R² = 0.9967); ▲ [Cl⁻Na₂SO₄]⁻ (m/z = 154) (R² = 0.9912); ○ [SO₄⁻]⁻ (m/z = 96) (R² = 0.9946); ◊ [Cl⁻SO₄]⁻ (m/z = 131) (R² = 0.9992); □ [Na₂SO₄]⁻ (m/z = 119) (R² = 0.9971).

The main reaction of [ClO₂⁻Na₂ClO₂]⁻ ion at m/z 157 leads to the ionic product at m/z 170, attributed to [ClO₂⁻Na₂SO₃]⁻, and a ClO⁻ radical species (Equation (6)). The CID mass spectrum of the ionic product at m/z 170 shows a major dissociation into SO₃⁻, which accounts for the [ClO₂⁻Na₂SO₃]⁻ structure (Figure S7). As in the case of Cl-clustered species [Cl⁻Na₂ClO₂]⁻, the main reaction of [ClO₂⁻Na₂ClO₂]⁻ consists of an oxygen ion transfer, resulting in a fast intracluster oxidation of SO₂. The rate constant k₆ is 6.26 × 10⁻¹⁰ (±30%) cm³ s⁻¹ mol⁻¹ (Table 3), and a branching ratio of 81.8% (Table 1). The intracluster formation of SO₃⁻ gives rise to a negatively charged product in which one of the two ClO₂⁻ moieties only played a spectator role, whereas the sodium cation is reasonably involved in the coordination of the ClO₂⁻ and SO₃⁻ anions. However, the presence of a residual ClO₂⁻ moiety in the product ion [ClO₂⁻Na₂SO₃]⁻ is responsible for the consecutive reactivity of this species, which is deeply discussed in the next paragraph (vide
The complete reactive scheme of $[\text{ClO}_2-\text{NaClO}_2]^-$, integrated with the reactivity of $[\text{ClO}_2-\text{NaSO}_3]^-$, is reported in the Supplementary Materials (Scheme S1), showing the complex and intricate reactivity of an only apparently simple species.

Table 3. Rate constants (cm$^3$ mol$^{-1}$ s$^{-1}$) for the reaction: $[\text{ClO}_2-\text{NaClO}_2]^-$ + SO$_2$. Only the most relevant rate constants are reported. OIT: oxygen ion transfer; OAT: oxygen atom transfer; DOT: double oxygen transfer; add: addition reaction.

| Reactivity | $k \times 10^{-10}$ cm$^3$ mol$^{-1}$ s$^{-1}$§ |
|------------|---------------------------------|
| OIT        | $k_6$                           |
|            | 6.26                            |
| OAT        | $k_7$                           |
|            | 0.364                           |
|            | $k_{7.1}$                       |
|            | 9.57                            |
| DOT        | $k_8$                           |
|            | 0.251                           |
|            | $k_9$                           |
|            | 0.417                           |
|            | $k_{10}$                        |
|            | 0.134                           |
|            | $k_{11}$                        |
|            | 0.222                           |
| SO$_2$ add | $k_{\text{SO}_2}$              |
|            | 0.574                           |

§ ±30%.

A second path, indeed a minor one, leads to an ionic product at $m/z$ 141 and SO$_2$ (Equation (7)), formed through an OAT from one of the two ClO$_2^-$ unit to SO$_2$. The branching ratio is only 4.8% (Table 1) and a rate constant $k_7$ of $3.64 \times 10^{-11}$ (±30%) cm$^3$ s$^{-1}$ mol$^{-1}$ (Table 3). The ionic product at $m/z$ 141, resembles an aggregate in which a ClO$_2^-$ anion and a ClO$^-$ reactive moiety are both coordinated to sodium cation, although its fragmentation into the ClO$_3^-$ species at $m/z$ 83 seems to account for a [Cl-Na-ClO$_3^-$] structure (Figure S8). Nonetheless, the [Cl-Na-ClO$_3^-$] ion obtained by spraying a NaCl/NaClO$_3$ (1:1) millimolar solution resulted to be not reactive towards SO$_2$ (Figure S9).

Therefore, it seems more likely to attribute the [ClO-NaClO$_2^-$] connectivity to the ion at $m/z$ 141 that rearranges to [Cl-NaClO$_3^-$] upon CID, thus demonstrating the interaction of sodium cation with the ClO$_2^-$ and ClO$^-$ anions, rather than Cl$^-$ and ClO$_2^-$ species. The presence of two potential reactive units, CIO and ClO$_2$, make the [ClO-NaClO$_2^-$] cluster ion quite reactive. The consecutive OAT process observed (Equation (7.1)) has a rate constant $k_{7.1}$ of $9.57 \times 10^{-10}$ (±30%) cm$^3$ s$^{-1}$ mol$^{-1}$ (Table 3), which is much higher than $k_7$ relative to the similar OAT process in Equation (7). Again, as for reactions 2 and 2.1, the reason lies in the different reactivity of the free chlorite and hypochlorite anions, the first undergoing faster OIT and the second faster OAT processes. The product ion at $m/z$ 125 corresponds to the [Cl-NaClO$_2^-$] species, as demonstrated by its characteristic fragmentation pattern and the distinctive reactivity discussed in the previous paragraph (Figures S10 and S11).

Four different DOT channels were reported for the [ClO$_2$-NaClO$_2^-$] parent ion. The first three pathways (Equations (8)–(10)) resemble those already described for the [Cl-NaClO$_3$]$^-$ ion (Equations (3)–(5)), as the same product ions at $m/z$ 154, 131, and 96 are respectively detected. The intracluster DOT processes reported in Equations (3) and (8) occurs with similar rate constants $k_3$ and $k_6$, regardless the ligand [NaCl] or [NaClO$_2$] attached to the ClO$_2^-$ moiety ($k_3 = 3.06$ vs. $k_6 = 2.51 \times 10^{-11}$ cm$^3$ s$^{-1}$ mol$^{-1}$). A significantly faster formation of the [ClSO$_4^-$] ion at $m/z$ 131 was reported for the [ClO$_2$-NaClO$_2^-$] parent species with respect to [Cl-NaClO$_3^-$] ($k_9 = 4.17$ vs. $k_4 = 1.47 \times 10^{-11}$ cm$^3$ s$^{-1}$ mol$^{-1}$). Again, the formation of the free [SO$_4^-$] product ion represents the lowest DOT process ($k_{10} = 1.34 \times 10^{-11}$ cm$^3$ s$^{-1}$ mol$^{-1}$). In addition, a fourth DOT channel was observed only for the [ClO$_2$-NaClO$_2^-$] parent ion which is worthy of note. In this case, the oxidation of SO$_2$ leads to the product at $m/z$ 119 with a rate constant $k_{11}$ of $2.22 \times 10^{-11}$ cm$^3$ s$^{-1}$ mol$^{-1}$ (Equation (11)) which subsequently adds a further SO$_2$ molecule with a $k_{\text{add}}$ of $5.74 \times 10^{-11}$ cm$^3$ s$^{-1}$ mol$^{-1}$ (Equation (11.1), Table 3). Although the structure of the ionic species at $m/z$ 119 could not be directly probed owing to its unproductive CID, a possible [Na-SO$_4^-$] formula can be reasonably supposed. The corresponding ion at $m/z$ 119 was
also obtained by electrospraying a solution of Na\textsubscript{2}SO\textsubscript{4} which, once isolated and reacted with SO\textsubscript{2}, gave a ligated [Na\textsubscript{2}SO\textsubscript{4}SO\textsubscript{2}^{-}] addition product with a rate constant consistent with \( k_{\text{add}} \) of Equation (11.1), thus confirming the identity of the parent species at \( m/z \) 119 (Figure S12). The [Na\textsubscript{2}SO\textsubscript{4}]\textsuperscript{-} formula accounts for the oxidation of the sulphur atom of sulphur dioxide and the eventual reduction of the chlorine atoms of the [ClO\textsubscript{2}−Na\textsubscript{2}ClO\textsubscript{2}]\textsuperscript{-} ion. Both the ClO\textsubscript{2}− units may be involved in the reaction, in which each ClO\textsubscript{2}− anion transfers an O− moiety to SO\textsubscript{2} giving rise to an SO\textsubscript{4}2− species and the release of two ClO− radicals. This hypothesis was confirmed by replacing one of the two ClO− anions with the similarly oxygenated, but intrinsically unreactive ClO\textsuperscript{2−} ion to obtain the [ClO\textsubscript{2}−Na−ClO\textsubscript{2}]− parent ion. When exposed to SO\textsubscript{2}, this species shows an intrinsic reactivity comparable to that of the [ClO\textsubscript{2}−Na−ClO\textsubscript{2}]− ion with the only exception of the product at \( m/z \) 119 that was not observed, thus highlighting the involvement of both ClO\textsubscript{2}− anions in the double O− transfer.

2.3. Reactivity of [SO\textsubscript{3}−Na−ClO\textsubscript{2}]− Cluster Anion

To better investigate the consecutive reactivity of the product ion at \( m/z \) 170, arising from the [ClO\textsubscript{2}−Na−ClO\textsubscript{2}]− parent species through Equation (6), the putative [ClO\textsubscript{2}−Na−SO\textsubscript{4}]− ion was isolated from the sequence 157 to 170 (M\textsuperscript{2+}-isolated) and separately reacted with SO\textsubscript{2}. The reactivity observed is illustrated in Scheme 3.

![Scheme 3. Reactivity scheme [ClO\textsubscript{2}−Na−SO\textsubscript{4}]− ions (\( m/z = 170 \)) with SO\textsubscript{2}. Oxygen transfer channels (OIT, OAT, DOT) and bimolecular rate constants are indicated for each reaction.](image)

The overall reaction shows a rate constant \( (k_{\text{dec}}) \) of \( 3.74 \times 10^{-10} \) (±30%) cm\textsuperscript{3} s\textsuperscript{-1} mol\textsuperscript{-1} and an efficiency of 33.0% at 298 K (Table 1). These values agree with those reported for the other [X−Na−ClO\textsubscript{2}]− parent species analysed and having a unique ClO\textsubscript{2}− reactive moiety (Table 1). Regarding, instead, the distribution of the three reaction paths, an even more pronounced increase of the DOT channels, accounting for a total amount of 22.7%, was observed (Table 1). The time progress of the reaction is described by the kinetic plot in Figure 5 and the rate constants of each pathway are reported in Table 4.
Table 4. Rate constants (cm$^3$ mol$^{-1}$ s$^{-1}$) for the reaction [ClO$_2$·Na·SO$_3$]$^-$ + SO$_2$. Only the most relevant rate constants are reported. OIT: oxygen ion transfer; OAT: oxygen atom transfer; DOT: double oxygen transfer; add: addition reaction.

| Reaction          | Rate Constant $k \times 10^{-10}$ cm$^3$ mol$^{-1}$ s$^{-1}$ $\pm$30% |
|-------------------|---------------------------------------------------------------|
| OIT               | $k_{12}$ 2.63 $\pm$0.167 $\times$ 10$^{-10}$ $k_{13}$ 2.60 $\pm$0.167 $\times$ 10$^{-11}$ $\pm$30% |
| OAT               | $k_{13.1}$ 0.260 $\pm$0.167 $\times$ 10$^{-11}$ $\pm$30% $k_{14}$ 0.222 $\pm$0.167 $\times$ 10$^{-11}$ $\pm$30% |
| DOT               | $k_{15}$ 1.09 $\pm$0.222 $\times$ 10$^{-10}$ $\pm$30% $k_{16}$ 0.457 $\pm$0.222 $\times$ 10$^{-11}$ $\pm$30% |
| SO$_2$ addition   | $k_{add}$ 0.494 $\pm$0.222 $\times$ 10$^{-11}$ $\pm$30% |

The intracluster OIT process (Equation (12)) proceeds quickly, showing a $k_{12}$ of 2.63 $\times$ 10$^{-10}$ (±30%) cm$^3$ s$^{-1}$ mol$^{-1}$ (Table 4) and leading to the formation of an ion at $m/z$ 183. Unfortunately, the CID mass spectrum of this species does not allow to distinguish between a [SO$_3$·Na·SO$_3$]$^-$ or a [Na·SO$_4$·SO$_2$]$^-$ structure (Figure S14), the latter already observed as a product of the DOT process involving the [ClO$_2$·Na·ClO$_2$]$^-$ parent ion. Nonetheless, based on the reactivity of naked ClO$_2^-$ and knowing that the SO$_3^-$ moiety is notoriously unreactive with SO$_2$, it is reasonable to suppose a [SO$_3$·Na·SO$_3$]$^-$ general formula for this species.

The [ClO$_2$·Na·SO$_3$]$^-$ parent ion is also involved in an OAT reaction proceeding with a $k_{13}$ of 2.60 $\times$ 10$^{-11}$ (±30%) cm$^3$ s$^{-1}$ mol$^{-1}$ and giving rise to an ion at $m/z$ 154 that is consistent with a [ClO·Na·SO$_3$]$^-$ structure. The consecutive OAT reactivity of this species leading to the ion at $m/z$ 138 (Equation (13.1); $k_{13.1} = 1.09 \times 10^{-10}$ (±30%) cm$^3$ s$^{-1}$ mol$^{-1}$, Table 4, Figure S11) accounts for the presence of the surrounding reactive ClO$^-$ moiety in [ClO·Na·SO$_3$]$^-$ ($m/z = 154$). When M$^3$-isolated into the ion trap by the sequence 170 to 154 and exposed to SO$_2$, the ionic species at $m/z$ 154 is only partially reactive towards this neutral gas. A portion of the ionic population at $m/z$ 154 survives
over time, hinting at the concomitant presence of the unreactive [Cl-Na-SO₄]⁻ species together with the [ClO₂-Na-SO₃]⁻ isobaric ion that is consumed in the consecutive reaction (Figure S15). The [Cl-Na-SO₄]⁻ species can reasonably arise from a direct intracluster DOT channel (Equation (13b)), as previously observed in analogous processes involving the [Cl-Na-ClO₂]⁻ and [ClO₂-Na-ClO₃]⁻ parent ions (Equations (3) and (8)). As a result, the O₂⁻ transfer from ClO₂⁻ to SO₂ triggers the release of a neutral SO₃ moiety according to the electron affinity values of the species involved in the reaction [27–34,65]. Unfortunately, it was not possible to independently measure k₁₃b, which is therefore included with that of the OAT transfer, k₁₃. As a consequence, the branching ratio of the OAT might be slightly overestimated, at the expense of that for the DOT process, which could therefore be underestimated. Two other DOT pathways reported in Equations (14) and (15) were also previously observed for the [Cl-Na-ClO₂]⁻ and [ClO₂-Na-ClO₃]⁻ parent clusters (Equations (4) and (9), Equations (5) and (10)). All these pathways show rather similar formation rate constants of the 10⁻¹¹ cm³ s⁻¹ mol⁻¹ order of magnitude (Table 4).

[ClO₂-Na-SO₃]⁻ also reacts with SO₂, leading to the [Na-SO₄]⁻ product ion at m/z 119 (Equation (16)). The reaction, showing a k₁₆ of 4.57 × 10⁻¹¹ cm³ s⁻¹ mol⁻¹, proceeds with an intracluster O₂⁻ transfer. Such unusual reactivity probably involves both the ClO₂⁻ anion that triggers a classic O₂⁻ transfer and the SO₃⁻ moiety that may be responsible for an electron transfer, giving rise to an SO₃²⁻ anion through a concerted rearrangement. As previously reported (Equation (11.1)), the consecutive addition of an SO₂ molecule to the [Na-SO₄]⁻ product ion is observed, thus confirming the identity of the ion at m/z 119.

Finally, as to the reactivity of higher species such as [(NaClO₂)ₙ-ClO₂]⁻, only the rate constant relative to cluster with n = 2 has been measured (Table 1), which does not appear to be affected by the number of additional NaClO₂ units compared to [ClO₂-Na-ClO₂]⁻. However, it was not possible to evaluate the branching ratio of the OIT, OAT and DOT processes of [(NaClO₂)₂-ClO₂]⁻, due to the low intensity signals relative to parent cluster ions, and to the complex array of peaks resulting from the reaction with SO₂.

3. Materials and Methods

Mass spectrometric experiments were carried out on an LTQ-XL linear ion-trap mass spectrometer (Thermo Fisher Scientific) that was in-house modified to perform ion-molecule reactions (IMR) [53]. Water-acetonitrile (1:1) solutions of NaClO₂ at millimolar concentrations were injected into the ESI (electrospray ionization) source of the instrument at a flow rate of 5 µL min⁻¹ via the on-board syringe pump and using nitrogen as sheath and auxiliary gas (flow rate = 11 and 2 arbitrary units respectively, a. u. -0.37 L min⁻¹). Other [ML-ClO₂]⁻ cluster anions (L = F, Br, I, ClO₂; M = Li, Na) investigated in this work were obtained from millimolar solutions of 1:1 ML and NaClO₂ salts dissolved in water-acetonitrile (1:1). To generate chlorite cluster ions and optimize the ion transmission, spray voltage was tuned in the 1.8–3.2 kV range, whereas the capillary temperature was set at 275 °C. The distribution of the ionic aggregates strictly depends on the capillary and tube lens voltage. Hence, these parameters were in turn optimized to increase the signal intensity of the parent ion under investigation.

Once generated, reagent ions were transferred to the vacuum region of the trap, mass-to-charge isolated and reacted with sulphur dioxide. Each reaction product was then mass selected by a further step of isolation, that is typical of MSⁿ experiments performed by Ion Trap mass spectrometers, and the consecutive reactivity of these species was probed towards SO₂ to unravel a complete reaction picture. Furthermore, the ionic reactants and products were structurally characterized by collision-induced dissociation (CID) experiments performed by increasing the energy of mass-selected ions in the presence of helium as collision gas (pressure of ca. 3 × 10⁻³ Torr). Depending on the species of interest, normalized collision energies ranging between 20% and 40% were typically applied with an activation time of 30 ms. Ions were isolated with a window of 1 m/z, and the Q value was optimized to ensure stable trapping fields for all the ionic species under investigation.
Sulphur dioxide was introduced into the trap through a deactivated fused silica capillary that enters the vacuum chamber from a 6.25 mm hole placed in the backside of the mass spectrometer. The pressure of the neutral gas was kept constant by a metering valve and measured by a Granville-Phillips Series 370 Stabil Ion Vacuum Gauge. Owing to the position of the Pirani gauge, the actual sulphur dioxide pressure was estimated after calibration of the pressure reading [66]. Typical pressures of SO$_2$ ranged between $1.1 \times 10^{-7}$ and $8.0 \times 10^{-7}$ Torr, the uncertainty was estimated to be $\pm 30\%$. The signals of the ionic reactant and products were monitored over time as a function of the neutral concentration and for each reaction time an average of 10 scan acquisitions was recorded. The normalized collision energy was set to zero and the activation Q value was optimized to ensure stable trapping fields for all the ions. Xcalibur 2.0.6 software was used to acquire all the displayed mass spectra.

All the reactions can be regarded as pseudo-first-order processes due to the excess of neutral gas relative to the reactant ion in the trap. DynaFit4 software package [67] was used to perform nonlinear least squares regression to simultaneously fit reactant and products concentration versus time. Experimental data from the kinetic analyses were fitted to a mathematical model consistent with the postulated reaction mechanism. To check the validity of the kinetic schemes, the obtained unimolecular rate constants were used to simulate the time progress of the reactions using the kinetic simulation function contained in DynaFit4. Bimolecular rate constants $k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$) were obtained dividing the pseudo-first-order constants (s$^{-1}$) by the concentration of neutral reagent gas. The branching ratios between the three channels (OIT, OAT, DOT) were calculated from the constants of formation of the primary direct products for each reactive species. The reaction efficiency was calculated as the ratio of the bimolecular rate constant $k$ to the collision rate constant ($k_{coll}$), according to the average dipole orientation (ADO) theory [68]. To ensure the accuracy of the $k$ values, approximately 15 independent measurements for each precursor ion were performed on different days over a sevenfold neutral pressure range. The standard deviation in the fitting parameters of the kinetic modelling used is usually evaluated between 10–20%, whereas the uncertainty attached to the measurement of the neutral pressure is typically evaluated $\pm 30\%$.

4. Conclusions

Mass spectrometry has been used to elucidate the gas-phase reactivity of [NaL·ClO$_2$]$^-$ cluster anions (L = ClO$_x^-$ with $x = 0–3$) with sulphur dioxide. These charged species can be taken as simplified models of large-scale reactions occurring in solution or in the flue-gas desulphurization processes, which are accomplished by sodium chlorite solutions. The kinetic analysis has shown that SO$_2$ was efficiently oxidised by oxygen atom transfer (OAT), oxygen ion transfer (OIT), and double oxygen transfer (DOT) respective to SO$_3^-$, SO$_3^{2-}$ and SO$_4^{2-}$. In the case of OIT and DOT processes, an intracluster reaction was observed, by which the oxidised ionic forms of SO$_2$, namely SO$_3^{2-}$ and SO$_4^{2-}$, remain within the cluster and are not released as a free species. The results here reported show that when ClO$_2^-$ is ligated to a non-redox active molecule, the complexation leads to a moderate reduction in the rate of oxidation processes, without substantially influencing the branching ratio. This effect contrasts, but not surprisingly, with what is observed in solution, where dissolved salts increase the SO$_2$ capture by increasing ionic strength of the solutions. In the gas phase, the direct and strong interaction of the chlorite anion with the ligand is detrimental to the reaction rate. However, the effect of redox active ligands, metallic or metal-free, could be quite different, as suggested by the reactivity observed with [ClO$_2^·$Na·ClO$_2$]$^-$, in which the second reactive ClO$_2^·$ moiety succeeds in increasing the rate of the oxidation. Therefore, the ligation with a redox active group, different from the chlorite one, could succeed in tuning the oxidation processes.
Supplementary Materials: The following are available online. Figure S1: Full-scan mass spectrum of a NaClO₂ salt solution; Figure S2: Ion-molecule reaction between isolated [ClNaClO₂]⁻ cluster ion and SO₂; Figure S3: CID mass spectrum of [ClNaSO₄]⁻ ion at m/z 138; Figure S4: CID mass spectrum of [ClNaSO₄]⁻ ion at m/z 154; Figure S5: CID mass spectrum of [ClSO₄]⁻ ion at m/z 131; Figure S6: ion-molecule reaction between isolated [ClO₂NaClO₂]⁻ cluster ion at m/z 157 SO₂; Figure S7: CID mass spectrum of [ClO₂NaSO₄]⁻ product ion at m/z 170; Figure S8: CID mass spectrum of (a) [ClO₂NaClO₂]⁻ product ion at m/z and (b) [ClNaClO₃]⁻ standard ion at m/z 141; Figure S9: mass spectrum of the ion-molecule reaction of (a) [ClO₂NaClO₂]⁻ ion at m/z and (b) [ClNaClO₃]⁻ standard ion at m/z 141 towards SO₂; Figure S10: mass spectrum of the ion-molecule reaction between [ClNaClO₂]⁻ consecutive product ion at m/z 125, MS²-isolated from the reaction sequence m/z 157 to m/z 141 to m/z 125 and SO₂; Figure S11: magnified plot of the kinetic reported in Figure 4; Figure S12: mass spectrum of the ion-molecule reaction of (a) [NaSO₄]⁻ product ion at m/z 119, MS²-isolated, and (b) [NaSO₄]⁻ standard ion at m/z 119 towards SO₂; Figure S13: mass spectrum of the ion-molecule reaction between [ClO₂NaSO₄]⁻ product ion at m/z 170; MS²-isolated from the reaction sequence m/z 157 to m/z 170 and SO₂; Figure S14: CID mass spectrum of product ion at m/z 183; Figure S15: ion-molecule reaction of (a) a mixed ionic population at m/z 154, MS²-isolated from the reaction sequence m/z 157 to m/z 170 to m/z 159 and (b) [ClNaSO₄]⁻ ion at m/z 154, MS²-isolated from the reaction of [ClNaClO₂]⁻ reactant ion towards SO₂; Figure S16: mass spectrum of the ion-molecule reaction between [NaSO₄]⁻ product ion at m/z 119 and SO₂; Scheme S1: Complete reaction sequences of [ClO₂NaClO₂]⁻ ion at m/z 157 and of its product ion [ClO₂NaSO₄]⁻ ion at m/z 170.

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