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Kinetics of the reaction of $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})_n$, $n = 0, 1, 2$, with nitric acid, a key reaction in tropospheric negative ion chemistry†

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A significant fraction of nitrate in the troposphere is formed in the reactions of HNO_3 with the carbonate radical anion $\text{CO}_3^{\bullet-}$ and the mono- and dihydrated species $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})_{1,2}$. A reaction mechanism was proposed in earlier flow reactor studies, which is investigated here in more detail by quantum chemical calculations and experimental reactivity studies of mass selected ions under ultra-high vacuum conditions. Bare $\text{CO}_3^{\bullet-}$ forms $\text{NO}_3^-(\text{OH}^{\bullet})$ as well as NO_3^- , with a total rate coefficient of $1.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})$ in addition affords stabilization of the $\text{NO}_3^-(\text{HCO}_3^{\bullet})$ collision complex, and thermalized $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})$ reacts with a total rate coefficient of $6.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. A second solvent molecule quenches the reaction, and only black-body radiation induced dissociation is observed for $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})_2$, with an upper limit of $6.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ for any potential bimolecular reaction channel. The rate coefficients obtained under ultra-high vacuum conditions are smaller than in the earlier flow reactor studies, due to the absence of stabilizing collisions, which also has a strong effect on the product branching ratio. Quantum chemical calculations corroborate the mechanism proposed by Möhler and Arnold. The reaction proceeds through a proton-transferred $\text{NO}_3^-(\text{HCO}_3^{\bullet})$ collision complex, which can rearrange to $\text{NO}_3^-(\text{OH}^{\bullet})(\text{CO}_2)$. The weakly bound CO_2 easily evaporates, followed by evaporation of the more strongly attached OH^{\bullet} , if sufficient energy is available.

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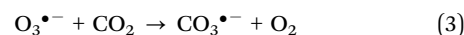
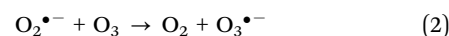
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Introduction

The $\text{CO}_3^{\bullet-}$ radical anion is an important intermediate in the tropospheric chemistry of anions.^{1,2} Quantitative modeling by Kawamoto *et al.*³ places the fractional abundance of $\text{CO}_3^{\bullet-}$ core ions in the troposphere in the range of 0.9–2.3%, quite comparable to HSO_4^- core ions close to the ground, while the overwhelming majority of negative ions have an NO_3^- core. However, a significant fraction of $\text{NO}_3^-(\text{H}_2\text{O})$ is formed in the reaction of $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})$ with HNO_3 .³ In recent years, ions in the troposphere have received increased attention in the form of charged aerosol particles.⁴ In a series of laboratory experiments, the CLOUD collaboration at CERN has recently shown that ions play an important role for aerosol nucleation and cloud formation in the troposphere.^{5–8}

The formation of $\text{CO}_3^{\bullet-}$ in atmospheric conditions was described by Fehsenfeld, Ferguson and co-workers in the 1970s.⁹ In the first step electrons react with O_2 and an additional collision partner M to form $\text{O}_2^{\bullet-}$, reaction (1). Ozonide $\text{O}_3^{\bullet-}$ is formed by charge transfer to an ozone molecule, reaction (2). The ozonide anion finally transfers O^- to a carbon dioxide molecule, forming $\text{CO}_3^{\bullet-}$ and O_2 , reaction (3).



The properties of $\text{CO}_3^{\bullet-}$ itself were intensively studied by spectroscopy. Matrix isolation techniques were applied by Jacox *et al.*,¹⁰ and a number of other groups used photodissociation techniques to characterize $\text{CO}_3^{\bullet-}$.^{11–14} The $\text{O}_2\text{C}-\text{O}^-$ bond dissociation energy was determined by Johnson, Viggiano and co-workers *via* photodissociation and high level quantum chemical calculations to be $269 \pm 5 \text{ kJ mol}^{-1}$.^{15–17}

Despite its key role in tropospheric anion chemistry,¹⁸ only a small number of gas phase reactions were studied.^{19–23} These are mostly reactions with nitrogen oxides, leading to formation

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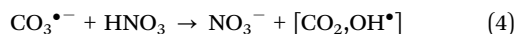
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7cp07773d



of nitrate NO_3^- .^{3,24–27} Reactions of $\text{CO}_3^-(\text{H}_2\text{O})_{0,1,2}$ with formic, acetic, propionic, butyric, glyoxylic, pyruvic and pinonic acid were investigated in a flow tube experiment by Arnold *et al.*^{28,29} They reported as initial step mostly proton transfer giving the deprotonated acids as products. For propionic acid and larger, they also observed clustering with $\text{CO}_3^{\bullet-}$ and formation of radical species, *e.g.* $\text{CH}_3\text{CH}(\bullet)\text{COO}^-$ from propionic acid.^{28,29} However, we recently showed that the reaction with formic acid proceeds mostly *via* oxidation of formic acid to carbon dioxide and water.³⁰ The deprotonation product HCOO^- was re-assigned to the reaction of formic acid with $\text{HCOO}^-(\text{OH}\bullet)$, an intermediate in the oxidation reaction that is formed in small concentrations.

A similar pattern emerged for the reaction of $\text{CO}_3^{\bullet-}$ with HCl. A flow tube study by Dotan *et al.*²⁴ established an upper limit for the rate of $3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, without observing any products. Recent studies in our laboratory reveal that this reaction proceeds *via* formation of a short lived, very reactive $\text{Cl}^-(\text{OH}\bullet)$ intermediate that reacts fast with a second HCl molecule, producing HCl_2^- and $\text{Cl}_2^{\bullet-}$ as final products.³¹ The rate of the first step is $4.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, consistent with the upper limit given by Dotan *et al.*²⁴ Interestingly, hydration dramatically accelerates the rate to $2.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})$, resulting in the reactive $\text{Cl}^-(\text{HCO}_3\bullet)$ radical species.³¹

Nitric acid^{21–23,32} and methane sulfonic acid²⁰ show efficient reactions with $\text{CO}_3^{\bullet-}$. The gas phase ion chemistry of HNO_3 was extensively investigated by Fehsenfeld and coworkers.²¹ They reported a reaction rate coefficient of $8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for reaction (4), measured by the flowing afterglow technique.



Möhler and Arnold investigated the reaction of HNO_3 with $\text{CO}_3^{\bullet-}$ and $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})$ in a flow-reactor triple quadrupole mass spectrometer in the presence of 1.7 mbar N_2 and 0.3 mbar O_2 as buffer gas.²² For bare $\text{CO}_3^{\bullet-}$ they observed NO_3^- , $[\text{NO}_3, \text{OH}\bullet]^-$ and $[\text{CO}_3\bullet, \text{HNO}_3]^-$ as primary products, followed by clustering reactions with HNO_3 .²² No $[\text{NO}_3, \text{OH}\bullet]^-$ was observed when 0.03 mbar H_2O was added to the buffer gas to study the hydrated species, while $[\text{CO}_3\bullet, \text{HNO}_3]^-$ was the dominant product.²² A mechanism *via* an excited collision complex $[(\text{CO}_3\bullet, \text{HNO}_3)]^*$ was proposed. The complex is de-excited by collisions, or decays into NO_3^- or $[\text{NO}_3, \text{OH}\bullet]^-$.²² Catoire and co-workers used the $\text{CO}_3^{\bullet-} + \text{HNO}_3$ reaction for testing their flowing afterglow setup and observed the same primary products as Möhler and Arnold.^{22,32} Since no mass selection was available for the reactant ions, the exact sequence of reactions generating the observed products, in particular the role of the $[\text{NO}_3, \text{OH}\bullet]^-$ and the influence of an additional water molecule on the reactivity, remained unclear.

Because of its central role in tropospheric negative ion chemistry,^{1,3} we investigated the reaction of $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})_n$, $n = 0, 1, 2$, with HNO_3 by FT-ICR mass spectrometry and quantum chemical calculations. Each cluster size was studied separately with mass-selected ions. The extremely low pressure in the FT-ICR instrument leads to product distributions different from the flow reactor studies, due to the absence of stabilizing collisions. A key problem in gas-phase reactivity studies with HNO_3 is the

inherent instability of this substance. HNO_3 decomposes in concentrated aqueous solutions. In earlier studies on the reactivity of ionic water clusters,^{33–35} we worked with aqueous concentrated solutions of HNO_3 , which yields a mixture of HNO_3 and H_2O in the reaction region, with traces of the decomposition product HONO. The observed reaction products confirmed that the abundance of HONO was less than 3% of the HNO_3 partial pressure. To identify reactions where HONO might play a role, we use quantum chemical calculations to identify thermochemically allowed reaction pathways. In addition, structural as well as thermochemical information is obtained for stationary points on the reaction potential energy surface. Together, a consistent picture of the reaction mechanism evolves.

Computational and experimental details

The ion–molecule reaction profiles were simulated with density functional theory at the M06-2X/6-311++G(d,p) level of theory employing the Gaussian09 program suite.³⁶ The energies of all optimized geometries were corrected with zero-point energy obtained from harmonic vibration analyses. Local minima and transition structures on the potential energy surface were confirmed with absence of and presence of one imaginary frequency, respectively. The local minima associated with each transition structure were verified by the intrinsic reaction coordinate (IRC) method. Spin density distributions were evaluated at the same level of theory and shown as isosurfaces at a value of 0.01 a.u. Table S1 in ESI† compares the used methods/basis sets with experimental values. The coordinates are given in Table S4 (ESI†).

The experiments were performed on a modified Bruker/Spectrospin CMS47X FT-ICR mass spectrometer as described in detail elsewhere.^{37–39} The spectrometer is equipped with a Bruker Infinity Cell, an APEX III data station, a 4.7 Tesla magnet and an external laser vaporization ion source. $\text{CO}_3^{\bullet-}$ was produced in the laser vaporization ion source^{39–42} *via* expansion of a helium/water/oxygen/carbon dioxide mixture using a zinc target for the production of electrons. As vaporization laser a frequency doubled Nd:YAG laser at a pulse energy of $\sim 5 \text{ mJ}$ at 10 Hz was used. All produced anionic species were transferred into the ICR cell, where they can be stored for several seconds or minutes. The ion of interest, $\text{CO}_3^{\bullet-}$ or $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})_{1,2}$, was then isolated *via* resonant excitation of unwanted ions prior to measuring the kinetics. A constant background pressure of HNO_3 and H_2O (concentrated aqueous solution, 70% HNO_3 , Sigma-Aldrich) was introduced into the ultrahigh vacuum region *via* a leak valve. Due to the inherent instability of HNO_3 , also traces of HONO were present, which are formed from the $\text{NO}_2\bullet$ decomposition product on thin films of H_2O and HNO_3 , as present in the vacuum system.⁴³ Mass spectra were taken after different reaction delays relative to the end of the fill and isolation cycle. The intensities were extracted from the mass spectra. A rate coefficient matrix defines the allowed reaction channels and the data was fitted using a genetic algorithm that optimizes the rates from the



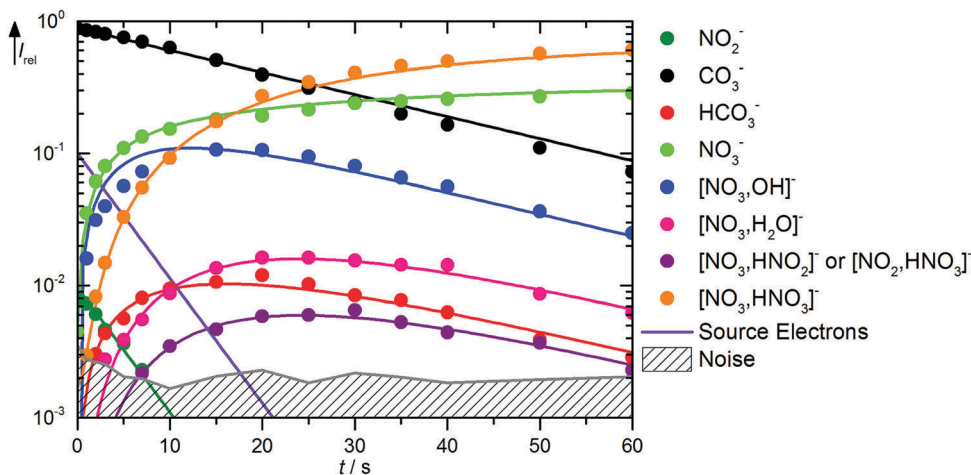


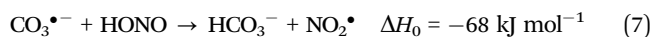
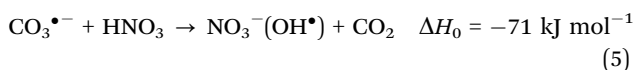
Fig. 2 Kinetics of the reaction of $\text{CO}_3^{\bullet-}$ with HNO_3 and H_2O , with traces of HONO, at a HNO_3 partial pressure of 1.4×10^{-8} mbar. The lines represent the fit with the rate coefficients from Table S1 (ESI[†]). Selected mass spectra are shown in Fig. S5 (ESI[†]).

Table 1 Bimolecular rate coefficients k_{abs} for the reactions discussed in the text

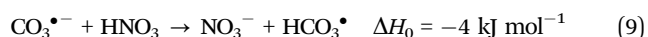
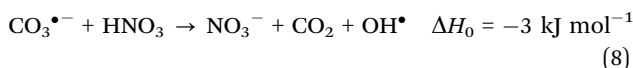
Reaction	Rate coefficient $k_{\text{abs}}/\text{cm}^3 \text{ s}^{-1}$
(5) $\text{CO}_3^{\bullet-} + \text{HNO}_3 \rightarrow \text{NO}_3^-(\text{OH}^{\bullet}) + \text{CO}_2$	8.9×10^{-11}
(8/9) $\text{CO}_3^{\bullet-} + \text{HNO}_3 \rightarrow \text{NO}_3^- + [\text{CO}_2, \text{OH}^{\bullet}]$	2.1×10^{-11}
(10) $\text{HCO}_3^- + \text{HNO}_3 \rightarrow \text{NO}_3^- + \text{CO}_2 + \text{H}_2\text{O}$	2.8×10^{-10}
(11) $\text{NO}_3^-(\text{OH}^{\bullet}) + \text{H}_2\text{O} \rightarrow \text{NO}_3^-(\text{H}_2\text{O}) + \text{OH}^{\bullet}$	1.2×10^{-10a}
(12) $\text{NO}_3^-(\text{OH}^{\bullet}) + \text{HNO}_3 \rightarrow \text{NO}_3^-(\text{H}_2\text{O}) + \text{NO}_3^{\bullet}$	5.3×10^{-11a}
(14) $\text{NO}_3^-(\text{OH}^{\bullet}) + \text{HNO}_3 \rightarrow \text{NO}_3^-(\text{HNO}_3) + \text{OH}^{\bullet}$	3.6×10^{-10}
(16) $\text{NO}_2^- + \text{HNO}_3 \rightarrow \text{NO}_3^- + \text{HONO}$	7.2×10^{-9}
(18) $\text{CO}_3^{\bullet-}(\text{H}_2\text{O}) + \text{HNO}_3 \rightarrow \text{NO}_3^-(\text{OH}^{\bullet}) + \text{CO}_2 + \text{H}_2\text{O}$	1.4×10^{-10b}
(19) $\text{CO}_3^{\bullet-}(\text{H}_2\text{O}) + \text{HNO}_3 \rightarrow \text{NO}_3^-(\text{HCO}_3^{\bullet}) + \text{H}_2\text{O}$	9.4×10^{-11c}
(20) $\text{CO}_3^{\bullet-}(\text{H}_2\text{O}) + \text{HNO}_3 \rightarrow \text{NO}_3^- + \text{CO}_2 + \text{OH}^{\bullet} + \text{H}_2\text{O}$	1.4×10^{-10b} 3.8×10^{-10b}

^a Assuming either reaction (11) or (12). ^b Thermalized fraction of $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})$. ^c Cold fraction of $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})$; the accuracy of the absolute rates is estimated to be $\pm 40\%$ due to uncertainties in the pressure determination.

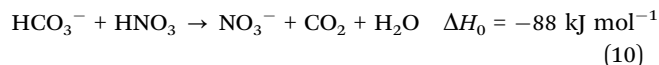
which is exothermic. The calculations show a barrierless HAT from HONO to $\text{CO}_3^{\bullet-}$. If we assume collision efficiency for reaction (7), a partial pressure below 1×10^{-10} mbar of the HONO background is sufficient to explain the observed abundance of HCO_3^- .



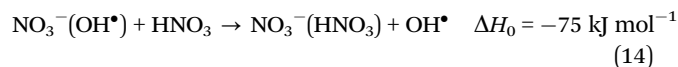
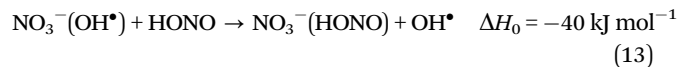
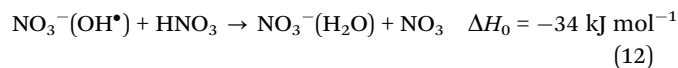
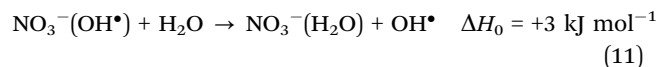
Formation of NO_3^- via reactions (8) or (9) with HNO_3 as neutral reactant is only slightly exothermic. Given that both reactants have low-lying vibrational modes, some extra thermal energy is available, which makes the reactions entirely plausible.



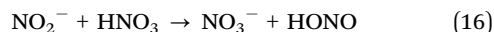
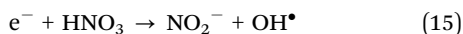
According to our kinetics fit, several secondary reactions are observed. HCO_3^- reacts to NO_3^- , most likely via a straightforward proton transfer from HNO_3 , reaction (10).



$\text{NO}_3^-(\text{OH}^{\bullet})$ either undergoes ligand exchange with H_2O or HAT from HNO_3 to form $\text{NO}_3^-(\text{H}_2\text{O})$, reactions (11) or (12), respectively. Ligand exchange is also possible with HONO as well as HNO_3 , reactions (13) and (14), respectively. Since reactions (12) and (14) compete with each other, with reaction (14) being both more exothermic and mechanistically favorable, ligand exchange with water is the most plausible origin of the $\text{NO}_3^-(\text{H}_2\text{O})$ product, reaction (11). Reaction (13) validates the presence of HONO in the reaction mixture.



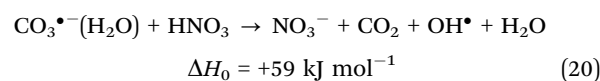
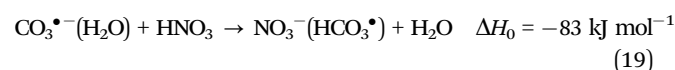
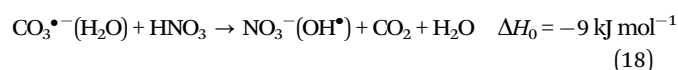
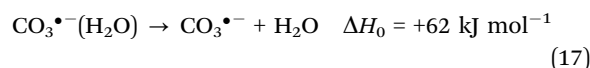
We also observe traces of NO_2^- , which are assigned to dissociative electron attachment. When working with negative ions, some free electrons are usually trapped in the ICR cell,⁴⁴ which react with HNO_3 according to reaction (15).²¹ In turn, NO_2^- is converted with near collision rate to NO_3^- *via* proton transfer from HNO_3 , reaction (16).



$\text{CO}_3^{\bullet-}(\text{H}_2\text{O})$. Fig. 3 shows the kinetics of the monohydrated species, mass spectra are displayed in Fig. S6 (ESI†). The scenario is quite complex, with a pronounced deviation of the $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})$ intensity from pseudo-first order behavior, for which a linear graph in the semi-logarithmic plot is expected. To describe the observed curvature, the population of this species is divided into two fractions, which correspond to the initially cold ions directly from the supersonic expansion, and the thermalized ions after heating by ambient black-body radiation and collision with the reaction gas. These effects are included in the kinetic model by allowing the cold fraction to be converted to the thermalized fraction, with a unimolecular rate treated as a fit parameter. Heating ultimately leads to formation of $\text{CO}_3^{\bullet-}$ *via* black-body infrared radiative dissociation (BIRD),^{45–58} reaction (17), with a lifetime of 3 s for the thermalized fraction. This reaction is not allowed for the cold fraction in the kinetic model, see Table S2 (ESI†). Since the major part of the $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})$ population is already thermalized at nominally $t = 0$ s, and the thermalized fraction reacts overall much faster than the cold fraction, the intensity drop of $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})$ is faster in the beginning, and levels off at later times because the conversion from the cold to the hot fraction becomes rate limiting, which explains the observed curvature.

The formation of $\text{NO}_3^-(\text{OH}^\bullet)$ is observed with an appreciable rate, and can be assigned to collisions with HNO_3 , reaction (18). Also the transition state for CO_2 formation is below the entrance channel, see Fig. 1, thus reaction (18) is fully consistent with

the calculations. The same is true for the ligand exchange product $\text{NO}_3^-(\text{HCO}_3^\bullet)$ formed *via* reaction (19). NO_3^- is exclusively formed from the thermalized fraction of $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})$ as a primary product in the kinetics. With HNO_3 as the reaction partner, reaction (20) is with $\Delta H_0 = +59 \text{ kJ mol}^{-1}$ significantly endothermic. However, the thermalized fraction of $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})$ already contains almost enough energy for dissociation. Together with the internal energy of the HNO_3 collision partner, the energy required for reaction (20) is available in the system. Reactions (18)–(20) yield a total rate coefficient of $6.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for the reaction of thermalized $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})$ with HNO_3 , 37% of the flow reactor value of $1.7 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ reported by Möhler and Arnold.²² All secondary reactions as well as NO_2^- formation *via* dissociative electron attachment proceed as discussed above.



$\text{CO}_3^{\bullet-}(\text{H}_2\text{O})_2$. Solvation of $\text{CO}_3^{\bullet-}$ with two water molecules leads to a significantly reduced reactivity with HNO_3 . The kinetics is shown in Fig. 4, mass spectra are available in Fig. S7 (ESI†). The major reaction channel is, as might be expected, loss of a water molecule due to BIRD, reaction (21). There is again formation of NO_2^- *via* reaction (15), but otherwise no primary products are observed from $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})_2$. The noise level of the kinetics, however, places a high upper limit of $6.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ on the rate coefficient for the direct reaction of $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})_2$ with HNO_3 . According to the thermochemical arguments discussed above, the most likely product of such a

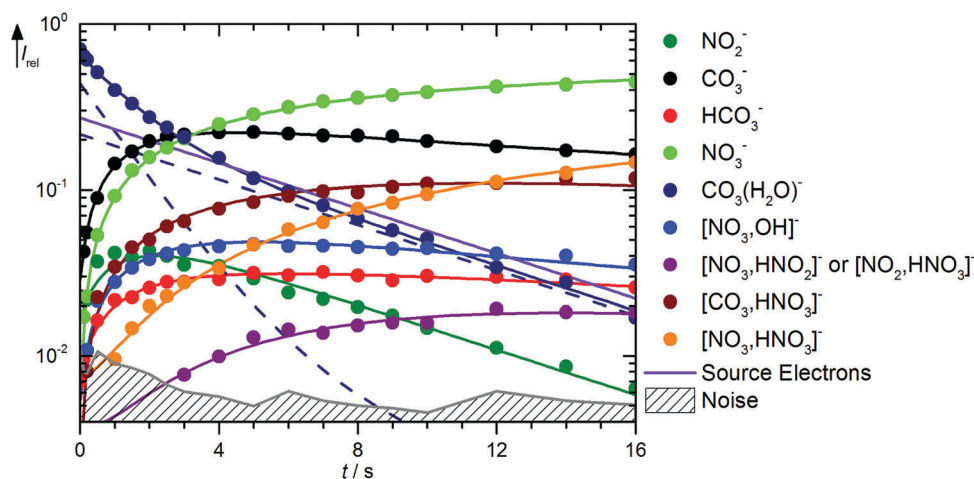


Fig. 3 Kinetics of the reaction of $\text{CO}_3^{\bullet-}(\text{H}_2\text{O})$ with HNO_3 and H_2O , with traces of HONO, at a HNO_3 partial pressure of 2.1×10^{-8} mbar. The lines represent the fit with the rate coefficients from Table S2 (ESI†). Selected mass spectra are shown in Fig. S6 (ESI†).



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