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Modelling iodide – iodate speciation in atmospheric aerosol: Contributions of inorganic and organic iodine chemistry

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Abstract. The speciation of iodine in atmospheric aerosol is currently poorly understood. Models predict negligible iodide concentrations but accumulation of iodate in aerosol, both of which is not confirmed by recent measurements. We present an updated aqueous phase iodine chemistry scheme for use in atmospheric chemistry models and discuss sensitivity studies with the marine boundary layer model MISTRA. These studies show that iodate can be reduced in acidic aerosol by inorganic reactions, i.e., iodate does not necessarily accumulate in particles. Furthermore, the transformation of particulate iodide to volatile iodine species likely has been overestimated in previous model studies due to negligence of collision-induced upper limits for the reaction rates. However, inorganic reaction cycles still do not seem to be sufficient to reproduce the observed range of iodide – iodate speciation in atmospheric aerosol. Therefore, we also investigate the effects of the recently suggested reaction of HOI with dissolved organic matter to produce iodide. If this reaction is fast enough to compete with the inorganic mechanism, it would not only directly lead to enhanced iodide concentrations but, indirectly via speed-up of the inorganic iodate reduction cycles, also to a decrease in iodate concentrations. Hence, according to our model studies, organic iodine chemistry, combined with inorganic reaction cycles, is able to reproduce observations. The presented chemistry cycles are highly dependent on pH and thus offer an explanation for the large observed variability of the iodide – iodate speciation in atmospheric aerosol.

1 Introduction

Atmospheric iodine chemistry has received increasing attention in recent years and large progress has been made re-

garding gas phase reaction kinetics (e.g. Joseph et al., 2005; Tucceri et al., 2006; Dillon et al., 2006; Plane et al., 2006), as well as regarding our understanding of iodine reaction cycles in the ambient air (e.g. Saiz-Lopez and Plane, 2004; Peters et al., 2005; Saiz-Lopez et al., 2006a,b) and related new particle production (e.g. Saunders and Plane, 2005; O'Dowd and Hoffmann, 2005; Saiz-Lopez et al., 2006a; Pechtl et al., 2006). However, several aspects of atmospheric iodine chemistry are still quite poorly understood, one of which is the speciation of iodine in atmospheric aerosol. As the aerosol phase is closely connected to the gas phase through uptake and release of iodine species, the understanding of reaction cycles within aerosols is relevant for the overall picture of atmospheric iodine chemistry.

Current models of atmospheric chemistry (Vogt et al., 1999; McFiggans et al., 2000) predict that the aerosol iodide (I^-) concentration is negligible (due to transformation into species that are released back to the gas phase) while iodate (IO_3^-) is believed to be inert and therefore accumulate in particles. In contrast, several observational data provide evidence for a non-negligible iodide content in aerosol samples (Gäbler and Heumann, 1993; Wimschneider and Heumann, 1995; Baker, 2004, 2005). Baker (2004, 2005) determined the speciation of soluble iodine (iodide, iodate, organic iodine) during two extended ship cruises in the Atlantic Ocean and found highly variable I^-/IO_3^- ratios. His measurements clearly show that the concentrations of iodide and iodate in aerosol are often of similar magnitude, that there are samples that do not contain iodate (but iodide), and that iodate is predominantly present in large aerosol ($>1\,\mu$m diameter). All these findings are not reproduced by current models. In this paper, we present an updated version of the aqueous phase chemistry scheme for use in atmospheric chemistry models. We suggest that iodate may be reduced via inorganic cycles, and the transformation of I^- into volatile iodine species may have been overestimated, both especially for acidic aerosol. Based on the idea of Baker (2005) we furthermore investigate

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Table 1. Aqueous phase iodine reactions. Differences to the mechanism used by Vogt et al. (1999) and von Glasow et al. (2002a) are highlighted in bold. H_2O is not written in the reactions.

No.	Reaction	n	upper limit	$k_0\ [(M^{1-n})\,s^{-1}]$	Reference
I 1+	$HOI+I^-+H^+\longrightarrow I_2$	3	yes*	4.4×10^{12}	Eigen and Kustin (1962)
I 1−	$\mathbf{I_2\longrightarrow HOI+I^-+H^+}$	**1**	yes*	**3.0**	**Eigen and Kustin (1962)[a]**
I 2+	$HOI+Cl^-+H^+\longrightarrow ICl$	3	yes*	2.9×10^{10}	Wang et al. (1989)
I 2−	$ICl\longrightarrow HOI+Cl^-+H^+$	1	yes*	2.4×10^6	Wang et al. (1989)
I 3+	$HOI+Br^-+H^+\longrightarrow IBr$	3	yes*	$\mathbf{4.1\times10^{12}}$	**Faria et al. (1993)**
I 3−	$IBr\longrightarrow HOI+H^++Br^-$	1	yes*	8.0×10^5	Faria et al. (1993)
I 4	$HOCl+I^-+H^+\longrightarrow ICl$	3	yes*	3.5×10^{11}	Nagy et al. (1988)*
I 5	$HOBr+I^-+H^+\longrightarrow IBr$	3	yes*	$\mathbf{1.2\times10^{13}}$	Troy and Margerum (1991)[b]
I 6	$IO+IO\longrightarrow HOI+\mathbf{HIO_2}$	2		1.5×10^9	Buxton et al. (1986)
I 7	$I^-+O_3\xrightarrow{H^+}HOI$	2		4.2×10^9	Magi et al. (1997)
I 8	$\mathbf{I^-+ICl\longrightarrow I_2+Cl^-}$	**2**		$\mathbf{1.1\times10^9}$	**Margerum et al. (1986)**
I 9+	$\mathbf{I^-+IBr\longrightarrow I_2+Br^-}$	**2**		$\mathbf{2.0\times10^9}$	**Faria et al. (1993)**
I 9−	$\mathbf{I_2+Br^-\longrightarrow I^-+IBr}$	**2**		$\mathbf{4.74\times10^3}$	**Faria et al. (1993)**
I 10	$HOI+Cl_2\longrightarrow HIO_2+2\,Cl^-+2H^+$	2		1.0×10^6	Lengyel et al. (1996)
I 11	$\mathbf{HOI+SO_3^{2-}\longrightarrow I^-+HSO_4^-}$	**2**		$\mathbf{5.0\times10^9}$	**assumed analogously to $HOBr+SO_3^{2-}$**
I 12	$\mathbf{HOI+HSO_3^-\longrightarrow I^-+HSO_4^-+H^+}$	**2**		$\mathbf{5.0\times10^9}$	**assumed analogously to I 11**
I 13	$HOI+HOCl\longrightarrow \mathbf{HIO_2}+Cl^-+H^+$	2		5.0×10^5	Citri and Epstein (1988)
I 14	$HOI+HOBr\longrightarrow \mathbf{HIO_2}+Br^-+H^+$	2		1.0×10^6	Chinake and Simoyi (1996)
I 15+	$\mathbf{HOI+HOI\longrightarrow HIO_2+I^-+H^+}$	**2**	yes*	$\mathbf{2.5\times10^1}$	**Schmitz (2004)**
I 15−	$\mathbf{HIO_2+I^-+H^+\longrightarrow 2HOI}$	**3**	yes*	$\mathbf{2.0\times10^{10}}$	**Edblom et al. (1987)**
I 16	$\mathbf{HIO_2+H_2O_2\longrightarrow IO_3^-+H^+}$	2		6.0×10^1	Furrow (1987)
I 17	$\mathbf{HIO_2+HOCl\longrightarrow IO_3^-+Cl^-+2H^+}$	2		1.5×10^3	Lengyel et al. (1996)
I 18	$\mathbf{HIO_2+HOBr\longrightarrow IO_3^-+Br^-+2H^+}$	2		1.0×10^6	Chinake and Simoyi (1996)
I 19+	$\mathbf{HIO_2+HOI\longrightarrow IO_3^-+I^-+2H^+}$	**2**		$\mathbf{2.4\times10^2}$	**Furrow (1987)**
I 19−	$\mathbf{IO_3^-+I^-+2\,H^+\longrightarrow HIO_2+HOI}$	**4**		$\mathbf{1.2\times10^3}$	**Schmitz (2000)**
I 20+	$\mathbf{HIO_2+I_2-H^+\longrightarrow IO_3^-+2I^-+2H^+}$	**1**		$\mathbf{5.5\times10^{-5}}$	**inferred from I1, I19, I20−**
I 20−	$\mathbf{IO_3^-+2I^-+2H^+\longrightarrow HIO_2+I_2-H^+}$	**5**		$\mathbf{4.2\times10^8}$	**Schmitz (2000)**
I 21	$\mathbf{I_2+HSO_3^-\longrightarrow 2I^-+HSO_4^-+2\,H^+}$	**2**		$\mathbf{1.7\times10^9}$	**Yiin and Margerum (1990)**
I 22	$\mathbf{HOI + DOM\longrightarrow I^-+H^++DOM}$	**2**		$\mathbf{10^5\ to\ 10^7}$	**estimated, see text; only used in ORG**

No.	Equilibrium reaction	m	n	$K_0\ [M^{n-m}]$	Reference
EQ1	$ICl+Cl^-\longleftrightarrow ICl_2^-$	2	1	7.7×10^1	Wang et al. (1989)
EQ2	$IBr+Br^-\longleftrightarrow IBr_2^-$	2	1	2.9×10^2	Troy et al. (1991)
EQ3	$ICl+Br^-\longleftrightarrow IClBr^-$	2	1	1.8×10^4	von Glasow et al. (2002a)
EQ4	$IBr+Cl^-\longleftrightarrow IClBr^-$	2	1	1.3	von Glasow et al. (2002a)

m, n give the order of the reaction. k_0 is the reaction rate constant for 298 K. K_0 is the equilibrium constant for 298 K.

* Special rate law for reactions controlled by diffusion as explained in the text.

[a] Although the back Reaction (I1−) is almost negligible compared to (I1+) for conditions of our simulations, we include it for completeness.

[b] Troy and Margerum (1991) do only provide a 2nd order reaction rate law that does not depend on the pH. However, in analogy to other $HOX+Y^-$ reactions we assume a pH-dependence of this reaction: We estimate the 3rd order reaction rate constants from the ratio of the 2nd order reaction rate constants of $HOBr + I^-$ and $HOCl+I^-$ (Troy and Margerum, 1991) and multiply this by the 3rd order reaction rate constant of Reaction (I4).

the effect of a possible reaction of HOI with dissolved organic matter (DOM) to produce iodide. In the next section, a detailed model description is provided. Results are presented and discussed in Sect. 3, while conclusions are drawn in Sect. 4.

2 Model description

For our studies we used the one-dimensional marine boundary layer model MISTRA, which has already been used for studies on gas phase iodine chemistry and new particle production from iodine oxides (von Glasow et al., 2002a; Pechtl

et al., 2006). The model comprises detailed aerosol microphysics and comprehensive chemistry both for the gas phase and the aqueous (aerosol) phase, which includes H-O-S-C-N-Cl-Br-I cycles, as well as exchange processes between the gas and the aqueous phase. The lowest 100 vertical model levels have an equidistant height of 10 m, the layers above 1000 m are spaced logarithmically. A thorough model description can be found in von Glasow et al. (2002a,b).

Concerning iodine chemistry, the model comprises the state-of-the-art gas phase reaction set of Pechtl et al. (2006), with updates of the reaction rate constants of the reactions $OIO+NO\longrightarrow IO+NO_2$ and $OIO+OH\longrightarrow HIO_3$ according to

Plane et al. (2006). Formation of new particles from iodine oxides (via OIO and I_xO_y) is also accounted for, using the parameterization developed by Pechtl et al. (2006) based on laboratory and model data by Burkholder et al. (2004). Freshly formed iodine particles are assumed to consist of non-volatile forms of iodine that do not participate in aqueous phase chemistry cycles.

The most detailed iodine scheme for the aqueous phase presently used in models of atmospheric chemistry was set up by Vogt et al. (1999) and since then has been adopted nearly unchanged for further studies (von Glasow et al., 2002a; Pechtl et al., 2006). The scheme accounts for the "recycling" of reactive iodine by the aqueous phase reactions of HOI with halide ions and the reactions of I^- with HOX (X=Cl, Br, I), which are especially fast in acidic aerosol. These "recycling" reactions lead to transformation of less reactive iodine species (HOI, I^-) to reactive iodine species (IX) that are re-emitted to the gas phase. The importance of this recycling process is supported by McFiggans et al. (2000) who found that observed gas-phase IO can only be reproduced by modelling if iodine recycling through aerosol is accounted for.

However, as already mentioned in the introduction, the scheme predicts negligible concentrations of I^- but accumulation of IO_3^- in particles, both of which is not supported by an increasing number of observations (Baker, 2004, 2005, as the most recent ones). Motivated by these obvious discrepancies, we found (after a thorough review of literature) that iodate might be reduced by pH-dependent reactions that are part of the complex system of the Dushman reaction (Dushman, 1904). The complicated kinetics of this reaction (net reaction: $IO_3^-+5I^-+6H^+\longrightarrow 3I_2+3H_2O$) has been subject of many studies for over a century (see e.g. Schmitz, 1999, 2000, for the present state of the art). Evidently, this reaction involves several individual steps and does not follow a simple rate law. For example, the order of the Dushman reaction depends on the I^- concentration (Schmitz, 2000): For I^- concentrations below about 5×10^{-7} M, the reaction rate depends linearly on $[I^-]$, for I^- concentrations above about 10^{-3} M the dependence is quadratic. Reactions (I19−) and (I20−) (Table 1) account for this finding: The rate of I20- (which depends quadratically on $[I^-]$) becomes larger than that of I19- (which depends linearly on $[I^-]$) for $[I^-]>3\times10^{-6}$ M.

Regarding the formation of HIO_2 by HOI+HOX (I13–I15, Table 1) for X=I the backward reaction is, under conditions encountered in atmospheric aerosol, much faster than the forward reaction. This leads to a net reduction of HIO_2 to HOI.

We only included IO_3^- and HIO_2 and not their corresponding acid or base (HIO_3 or IO_2^-). Due to their pKa values of 0.8 for HIO_3/IO_3^- (Strong and Pethybridge, 1987) and 6 for HIO_2/IO_2^- (our estimate), IO_3^- and HIO_2 are the most common forms for most pH values that are relevant for atmospheric aerosol. Including the equilibria would not be

sensible regarding the current state of knowledge, where no information is available about possible differences in reaction rates involving either the dissociated or the undissociated compound.

Furthermore, we introduced upper limits for the Reactions (I1–I5) (Table 1) towards low pH values, based on the fact that two species can never react with a rate larger than their encounter frequency. For example, for a pH of 2 (i.e. $[H^+]$=0.01 M) the rate of Reaction (I1) is 4.4×10^{10} [HOI] $[I^-]$ (after Eigen and Kustin's rate law, Table 1), but the encounter frequency between HOI and I^- is only about 5×10^9 M^{-1} s^{-1} which is an approximate value for diffusion-controlled rate constants.

The mechanism and rate laws of reaction I1 at different acidities are discussed in details in Schmitz (2004). In acidic or slightly acidic solutions, the rate law can be written:

$$\frac{k_+[HOX][Y^-][H^+]-k_-[XY]}{1+\alpha[H^+]}$$

The rate constants in the forward and backward directions, k_+ and k_-, are related to the equilibrium constant K_{eq} by $k_+/k_- = K_{eq}$ and α is such that $k_+/\alpha = k_{diff}$ is the rate constant of a diffusion-controlled reaction. At low $[H^+]$, the rate law of the forward reaction converges to the accepted 3rd order rate law while at high $[H^+]$ it converges to the highest possible value k_{diff} [HOX] $[Y^-]$. For the theory of diffusion-controlled reactions we refer the reader to general text books of chemical kinetics, e.g. Espenson (1995). We have used the same formulation for the reactions in Table 1 noted "upper limit: yes" and also for not listed reactions that do not involve iodine species (X, Y = Br, Cl). The experimental values of k_{diff} are usually unknown and we have used the accepted approximate value for this kind of reactions involving at least one uncharged species in water, $k_{diff} = 5\times10^9$ M^{-1} s^{-1} .

In addition to the equilibrium reactions EQ1–EQ4 introduced by von Glasow et al. (2002a), we included the reaction of I^- with ICl and IBr (I8, I9), which tend to oxidise iodide to molecular iodine. Furthermore, we add the reactions of HOI with SO_3^{2-} and HSO_3^- (I11, I12), although they have not been measured yet: HOI is usually a more powerful I^+ donor than I_2, i.e., Reaction (I12) should be faster than Reaction (I21). Also, the reaction rate constant of HOBr+SO_3^{2-} (5.0×10^9 M^{-1} s^{-1}, Troy and Margerum, 1991), is larger than the reaction rate constant of HOCl+SO_3^{2-} (7.6×10^8 M^{-1} s^{-1}, Fogelman et al., 1989), suggesting that HOI+SO_3^{2-} should even be faster. From these information (and knowing that the 2nd order rate constant cannot be larger than the diffusion-controlled limit) we assume rate constants of 5.0×10^9 for Reactions (I11) and (I12). Beside the reduction of iodate by iodide, we have also considered its reduction by sulfite. Gaspar and Showalter (1987) have adopted the simple rate law r(IO_3^- + HSO_3^-) = k $[IO_3^-][HSO_3^-]$ with k = 0.25 $M^{-1}s^{-1}$. Edblom et al. (1987) and Luo and Epstein (1989a) have used the same rate law

Table 2. Description of the model runs. For the sensitivity studies, the difference to BASE is described.

Model run	Description
BASE	base run including the full aqueous phase iodine chemistry scheme
OLD	without upper limits for I1-I5; without Reactions I8, I9, I11, I12, I15, I19, I20
NOUP	without uptake of HIO_3 from the gas phase
ORG	including the reduction of HOI to I^- by reaction with DOM I22
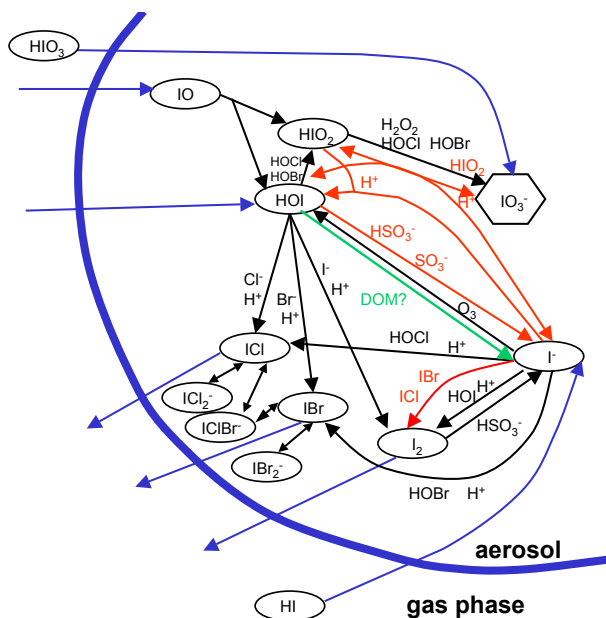
Fig. 1. Scheme of aqueous phase iodine chemistry as implemented in MISTRA. For reactions with + and − directions, only the dominant direction is indicated for the conditions of our model simulations where possible. Additional reactions compared to the Vogt et al. (1999) scheme are highlighted in red.

with k = 0.30 $M^{-1}s^{-1}$. This value was corrected later to k = 0.42 $M^{-1}s^{-1}$ (Luo and Epstein, 1989b). With these values, the reduction of iodate by sulfite has no significant consequence on our results, even for the almost neutral aerosols. The use of the more complicated rate law adopted by Rabai and Beck (1988) and by Rabai et al. (1995) would not change this conclusion. As the rate of this reaction is uncertain but negligible, we have not included it in the final reaction mechanism.

In Table 1, all reactions of our aqueous phase iodine chemistry scheme are summarized, where the modifications with respect to the Vogt et al. (1999) scheme are highlighted in bold. A schematic of our aqueous phase iodine mechanism is shown in Fig. 1. The complete chemical mechanism (except for the modifications presented here) can be found as electronic supplement to Pechtl et al. (2006).

The meteorology in the model was set up to represent mid-latitude summer conditions (43° N with a solar declination of 20°, i.e., end of July). The initial conditions are chosen such that no clouds form and the boundary layer height is about 700 m, where moisture and heat fluxes form the surface are adjusted to yield a constant boundary layer height. The near-surface temperature is about 16°C, the humidity increases from about 65% near the surface to about 90% near the boundary layer top.

After a 2-day spin up of the meteorology, model runs including the full chemistry scheme are run for 5 days. We concentrate on a clean marine environment, prescribing initial concentrations as in Pechtl et al. (2006). Regarding the iodine source, we assume a "background" open ocean source of organohalogens (CH_3I, CH_2ClI, CH_2I_2) prescribing surface fluxes after Vogt et al. (1999) and I_2 after Garland and Curtis (1981). The resulting maximum near-surface mixing ratios are about 2 pmol mol^{-1} (CH_3I), 1 pmol mol^{-1} (CH_2ClI, CH_2I_2) and 0.07 pmol mol^{-1} (I_2), where the maxima are reached shortly before sunrise. Gas phase IO and OIO mixing ratios are both about 0.1 pmol mol^{-1} during daytime and approximately zero during nighttime. Please note that the concentrations of reactive iodine species in our model are far below the values measured in coastal regions (Alicke et al., 1999; Allan et al., 2001; Saiz-Lopez and Plane, 2004; Peters et al., 2005; Saiz-Lopez et al., 2006b), as we are trying to reproduce clean open ocean conditions.

We assume a typical marine background aerosol size distribution (Hoppel and Frick, 1990) and distinguish between "sulfate" aerosol (dry aerosol radius <0.5 μm; initial composition 99.6% $(NH_4)_2SO_4$, 0.4% NH_4NO_3) and "seasalt" aerosol (dry radius >0.5 μm; initial composition like sea water, initial pH like surface ocean water). The production of seasalt aerosol via bursting bubbles at the sea surface is computed using the parameterization of Monahan et al. (1986). As the relative humidity remains above the crystallisation humidity of both seasalt and sulfate particles all aerosol particles are deliquesced in the model runs at all times. The different model runs that are compared in the present study are listed in Table 2. Except for the base case described above (BASE) we perform a model run utilizing the "old" liquid phase iodine scheme that resembles the scheme used
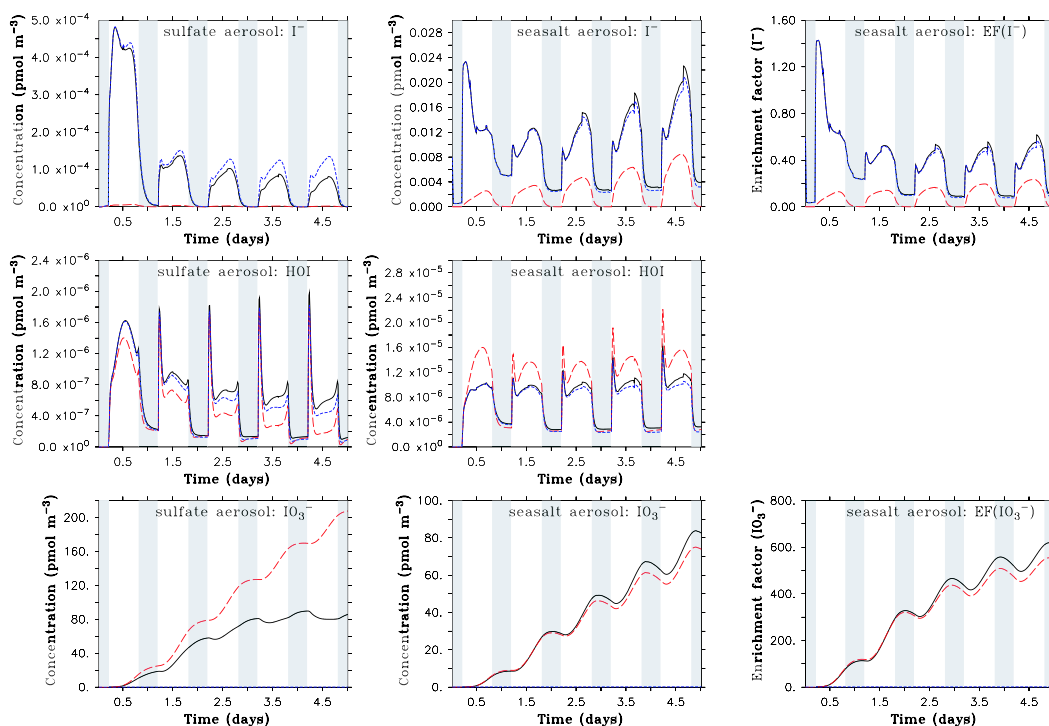
Fig. 2. 5-days timeseries of several aqueous phase iodine species and iodine enrichment factors (EF) in 15 m altitude for BASE (black, solid), OLD (red, dashed) and NOUP (blue, dotted). Simulations start at midnight. Concentrations are given in pmol m^{-3}(air). Nighttime periods are grey-shaded.

by Vogt et al. (1999), von Glasow et al. (2002a), Pechtl et al. (2006) (OLD). We also compare with a run where the uptake of HIO$_3$ (which forms via OIO+OH) from the gas phase is prohibited (NOUP). Finally, in ORG we assume iodide production by the reaction of HOI with DOM as suggested by Baker (2005) and elucidate the impact on I$^-$ and IO$_3^-$ concentrations. In this case, we assume that organic matter is emitted from the ocean as part of the seasalt aerosol during bubble bursting. For the "sulfate" aerosol, we prescribe an initial organic fraction of 10%. Further information on the respective model sensitivity studies is provided later.

3 Results and discussion

3.1 Effects of the new chemistry scheme

During two extended ship cruises in the Atlantic Ocean Baker (2004, 2005) detected both iodide and iodate in most aerosol samples in strongly varying concentrations. Maximum values were about 10 pmol m^{-3}(air) for I$^-$ and about 50 pmol m^{-3}(air) for IO$_3^-$. In addition, Baker (2005) inferred from the difference between total soluble iodine and iodide + iodate that organic iodine species constitute with up to about 40 pmol m^{-3}(air) a significant fraction of particulate iodine. In the OLD model configuration, maximum near-surface iodide concentrations are 2×10^{-6} pmol m^{-3} for the

sulfate aerosol and 8×10^{-3} pmol m^{-3} for the seasalt aerosol (Fig. 2, red lines), which is both significantly below the values measured by Baker (2005) (note that all concentrations are given in pmol m^{-3}(air), i.e., in pseudo-gas phase concentrations). The smaller I$^-$ concentrations of the sulfate compared to the seasalt aerosol are due to the lower pH values of the first, leading to a faster consumption of iodide via the pH-dependent Reactions (I1–I5).

In contrast to iodide, iodate, which has no chemical sink in OLD, is accumulated in the model and reaches after 5 days values up to about 200 pmol m^{-3} for the sulfate and 85 pmol m^{-3} for the seasalt aerosols. The comparison with NOUP (blue lines in Fig. 2) shows that the main source of aerosol IO$_3^-$ is uptake of HIO$_3$ from the gas phase. Hence, in the model iodate accumulates faster in the small sulfate aerosols with a larger surface-to-volume ratio compared to the seasalt particles. The model simulation OLD exceeds the maximum measured IO$_3^-$ values by a factor of 4 and does not offer an explanation for near-zero iodate concentrations which were sometimes encountered during the ship cruises (especially in the fine aerosol fraction).

Including the "new" chemistry in the model (BASE, black lines in Fig. 2) improves the agreement between model and measurement, especially for the acidic sulfate aerosol (pH around 0.5): The introduced upper limits of the reaction rates for Reactions (I1–I5) increase the modelled I$^-$
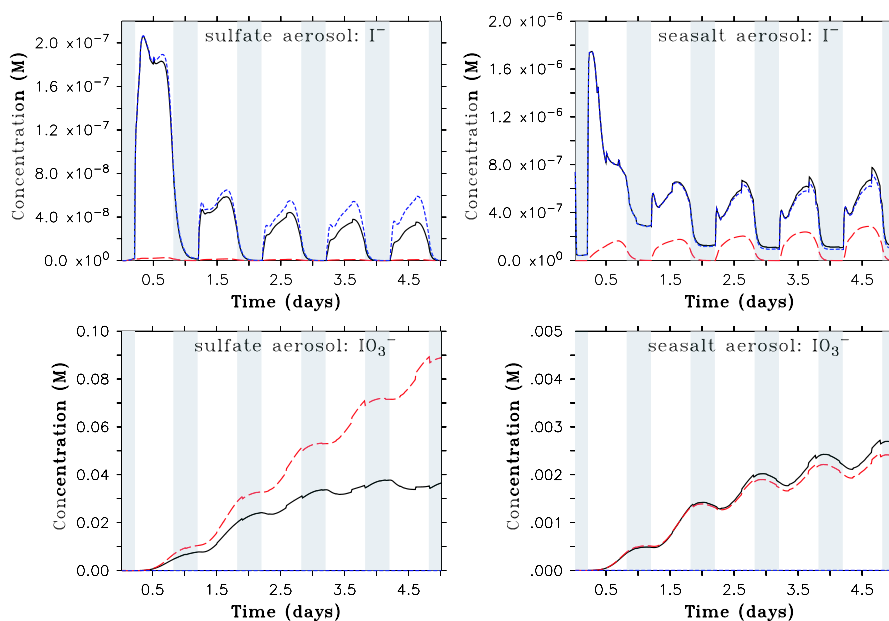
Fig. 3. As Fig. 2, but concentrations are given in $mol \, l^{-1}$ aqueous solution.

concentrations by about two orders of magnitude. The io-
dide taken up from the gas phase is oxidised more slowly
through these reactions which increases the rate of the Dush-
man reaction. The IO_3^- concentrations are almost stabilized
around $80 \, pmol \, m^{-3}$, mainly due to Reaction (I19−) (and a
smaller contribution of I20−) which both lead to a reduction
of IO_3^-. For BASE, the reaction rate of (I19−) is of simi-
lar magnitude as the uptake of gas phase HIO_3, leading to
the mentioned stabilization of iodate concentrations in the
sulfate aerosol. In this context, please note that the forma-
tion of HIO_3 in the gas phase (by reaction of OIO with OH)
and its subsequent uptake is itself highly uncertain, affecting
of course the accumulation behavior of IO_3^- in the aerosol.
The point is, however, that Reaction (I19−) constitutes an
efficient sink for iodate and therefore is able to prevent its
accumulation in acidic aerosol.

For the modelled seasalt aerosol (with a pH around 6
within the lowest 50 m), the reaction rates for Reactions (I1–
I5) are always below the upper limits determined by the en-
counter frequency, which hence do not increase I^- concen-
trations compared to OLD. The increase in I^- visible from
Fig. 2 is due to Reactions (I11) and especially (I12) which
convert HOI into I^-.

In seasalt aerosol, Reactions (I19−) and (I20−) are neg-
ligibly slow due to the low H^+ concentration (note the
quadratic dependence of the reaction rates of (I19−) and
(I20−) on [H^+]), and thus do not lead to a reduction of IO_3^-.
The rates of Reactions (I19+) and (I20+) are slightly larger
than those of (I19−) and (I20−), but are too small to visi-
bly increase iodate compared to OLD. The increase in IO_3^-
visible from Fig. 2 is rather an indirect consequence of Re-
actions (I19−), (I20−) occurring in the sulfate aerosol (not

shown): There, these iodate reduction reactions cause an in-
crease in aqueous phase HOI and I_2, leading (for HOI via
I1–I3) to enhanced release of I_2, IBr and ICl to the gas phase.
During daytime, these species photolyse, producing I rad-
icals and slightly increasing nearly all iodine species in the
gas phase. Among these is also HIO_3 which is taken up again
by particles and increases the concentration of IO_3^- there.
While for the sulfate aerosol, the enhanced uptake from the
gas-phase is over-compensated by iodate reduction (I19−,
I20−), it leads to a net increase in iodate concentrations in
case of the seasalt aerosol.

The importance of the coupling between gas- and aque-
ous phase is also evident from the distinct diurnal cycle of
iodide with pronounced minima during night: In the absence
of sunlight, photolytic processes (esp. in the gas phase) do
not occur while recycling processes in the aerosol, which do
not depend on sunlight, continue. Consequently, production
of gas phase iodine compounds that can be taken up by the
aerosol (esp. HI and HIO_3) stops while the liberation of IX
(X=I, Br, Cl) to the gas phase continues, leading to respective
minima in the aqueous phase.

The iodine enrichment factor (which is defined as the
I^-/Na^+ ratio in aerosol divided by that in seawater) is cal-
culated only for the seasalt aerosol since the sulfate aerosol
does not contain Na^+. For I^-, the enrichment factor is (even
including the new chemistry) mostly <1, i.e., the model pre-
dicts depletion of particulate iodide compared to seawater,
while it predicts enrichment of iodate up to a factor of 600.
This value is well within the range given by Baker (2005) for
total iodine enrichment, but the speciation between iodide
and iodate is still not captured by the model.

Figure 3 shows iodide and iodate concentrations in $mol \, l^{-1}$
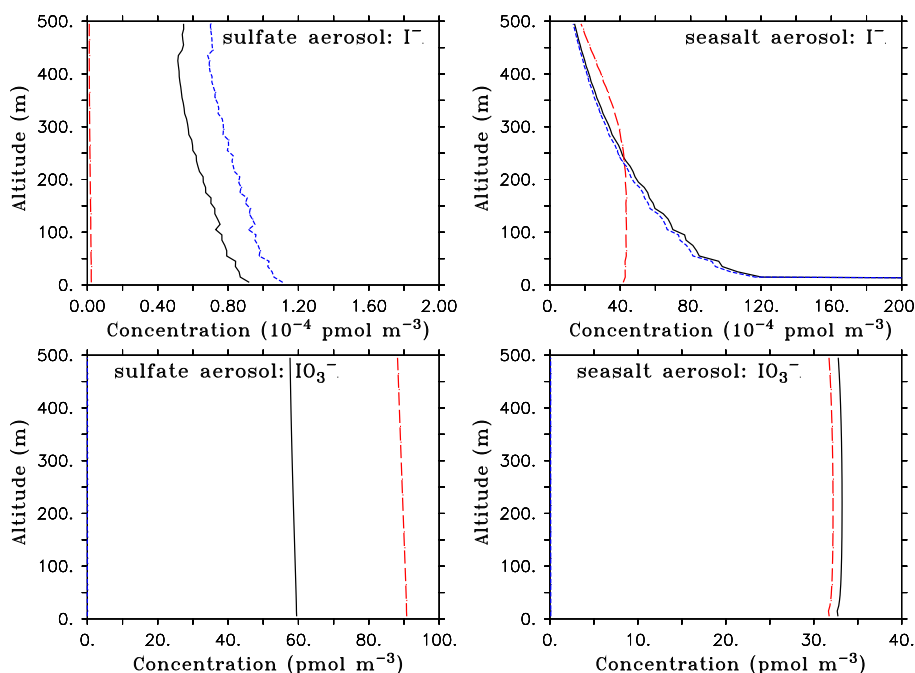
Fig. 4. Vertical profile of aqueous phase iodide and iodate at noon of model day 3 for BASE (black, solid), OLD (red, dashed) and NOUP (blue, dotted).

aqueous solution (M) in addition to the pseudo-gas phase concentration mol m^{-3}(air) given in Fig. 2. This additional information may facilitate comparison with future measurements.

The modelled vertical gradients of iodide and iodate (again in pseudo-gas phase concentrations) are quite weak in the lowest couple of hundred meters, as shown exemplarily for noon of the third model day (Fig. 4). That is, the results discussed for the surface-near layers do mostly hold for higher altitudes as well. An exception is the pronounced vertical gradient of seasalt I$^-$ in the BASE case in the lowest 100 m that is caused by the increasing importance of Reactions (I11) and (I12) with decreasing altitude (due to a strong gradient in HSO$_3^-$ and SO$_3^{2-}$ mixing ratios). Near the surface, I$^-$ mixing ratios reach up to about 0.1 pmol mol^{-1}. The slightly lower seasalt I$^-$ mixing ratios above about 250 m in BASE compared to OLD results from iodide reduction by (I8) and (I9). From measurements, no information about vertical gradients in aerosol iodide and iodate is available yet, but would be certainly desirable for a thorough comparison.

As becomes immediately clear from Table 1, the aerosol pH is a crucial quantity not only for the recycling Reactions (I1–I5) but also for the reduction of HIO$_2$ (I15−) and IO$_3^-$ (I19−, I20−). While (I1–I3) and (I15) have a preferred direction for the whole range of pH values (I1–I3 in "+"-direction, I15 in "−"-direction), this is not the case for (I19) and (I20). Figure 5 shows, for the seasalt aerosol (BASE), both the actual pH values and its difference to the pH at which (I19) and (I20) are in equilibrium under the given con-

centrations for the iodine species ("pH$_{equil}$"). For pH-values smaller than pH$_{equil}$ (that is, pH−pH$_{equil}$<0), the direction of the reaction is such that it consumes H$^+$, i.e., leads to a reduction of IO$_3^-$. For Reaction (I19), this is the case only above roughly 100 m (middle panel of Fig. 5), while for Reaction (I20), it is the case already very close to the ground (lower panel of Fig. 5). As a consequence, for the seasalt aerosol of the BASE case (where the reaction rate of I19 is greater than that of I20) IO$_3^-$ is produced below and destroyed above about 100 m altitude.

For BASE, this finding is mostly of theoretical interest, since for the seasalt aerosol (I19) is much slower than the uptake of HIO$_3$ from the gas phase (see above). However, BASE is still associated with some deficiencies and uncertainties: First, the modelled I$^-$ concentration in seasalt aerosol is still about two orders of magnitude smaller than observed for both the coarse and the fine aerosol mode (Baker, 2005). Second, the uptake from the gas phase is quantitatively very uncertain (see above). For higher I$^-$ concentrations and smaller uptake, IO$_3^-$ reduction via (I19−) and (I20−) (which depends on [I$^-$]) would increase while IO$_3^-$ accumulation via uptake would decrease. Thus, the importance of Reactions (I19) and (I20) for the iodate balance could be significantly enhanced even in almost neutral aerosol.

The results of the BASE case can almost identically be reproduced with a reduced chemical mechanism that includes only Reactions (I1+), (I2) to (I5), (I7), (I8), (I9+), (I11), (I12), (I15−), (I16) and (I19−). For the acidic sulfate
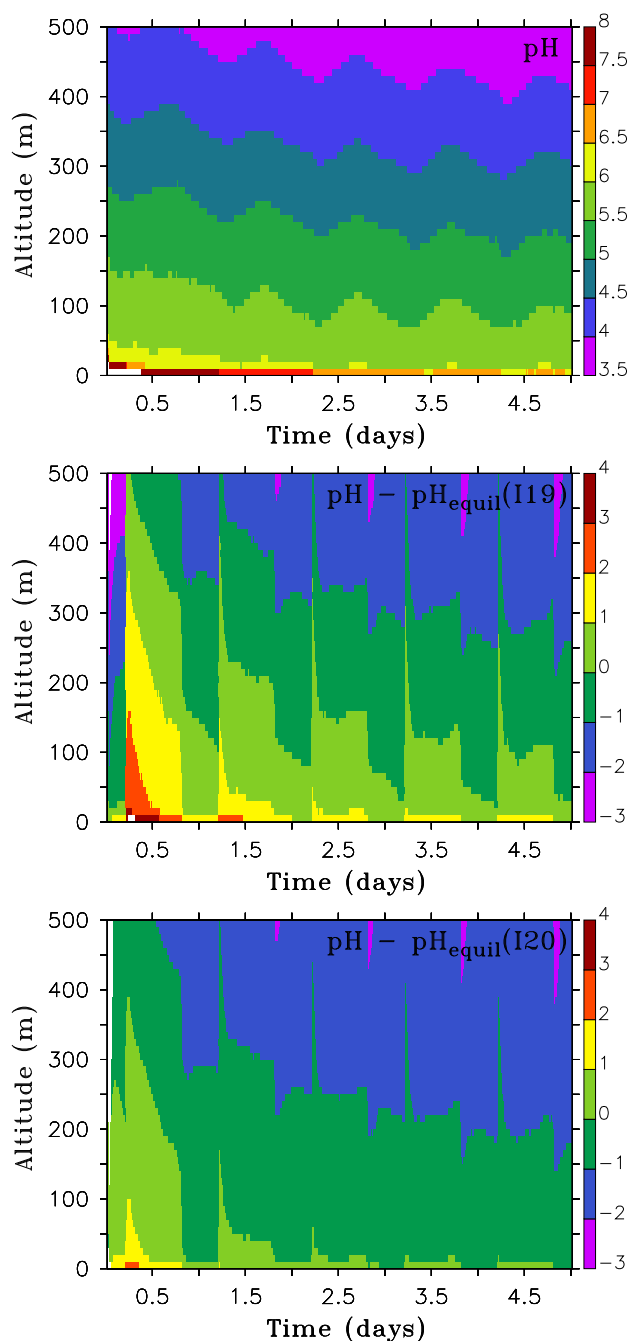
Fig. 5. PH of seasalt aerosol (upper panel). Difference between pH and equilibrium pH (definition see text) for Reactions (I19) (middle panel) and (I20) (lower panel) calculated from given concentrations of iodine species (BASE simulation).

aerosol, an even more reduced mechanism can be applied, excluding additionally (I7), (I8), (I9+), (I11), (I12) and (I16) (i.e., the remaining chemistry scheme comprises only the Reactions (I1+), (I2) to (I5), (I15−), and (I19−)). This information may be useful for setting up simplified model studies, but should be applied with caution as the importance of reac-

tions might significantly change under different ambient or chemical conditions or modified gas–liquid phase exchange.

In sum, the new reaction set of BASE compared to OLD leads to an improvement both in iodine and iodate in case of the acidic sulfate aerosol, but does only slightly affect the almost neutral seasalt aerosol (except for iodide in the lowest 100 m altitude). We have presented an inorganic chemical mechanism that offers the possibility to reduce iodate in acidic media and to restrict transformation of iodide into volatile iodine species. However, iodide concentrations are still one to three orders of magnitude lower than observations. It appears that pure inorganic chemistry is not sufficient to reproduce the observations. According to Baker (2005), who inferred the existence of soluble organic iodine species from his measurements, there is indeed evidence for organic iodine chemistry going on in the aqueous phase. In the following section, we discuss the possible role of dissolved organic matter (DOM) for enhancing iodide concentrations in atmospheric aerosol.

3.2 Iodide production by reactions involving DOM?

Unfortunately, very little is presently known about atmospheric organic iodine chemistry. However, some studies hint at a correlation of iodine with organics in atmospheric aerosol particles (Murphy et al., 1997; Middlebrook et al., 1998). In general, the presence of organic material especially in submicrometer marine aerosol appears to be a relatively abundant phenomenon (O'Dowd et al., 2004; Cavalli et al., 2004). Also, there is evidence that various organic compounds have the potential to reduce HOI or I_2 in seawater to I^- (Truesdale, 1974; Luther et al., 1995; Truesdale and Luther, 1995; Truesdale et al., 1995a,b). Baker (2005) proposed that the reaction of HOI with organic matter may be a significant source for soluble organic iodine in aerosol, and that the subsequent decay may provide a route for the formation of aerosol I^-. Evidence for the formation of iodocarbons via aqueous phase reactions of HOI with organic material was also provided by Carpenter et al. (2005).

Based on these studies, we investigated the possible formation of I^- by direct reaction of HOI with dissolved organic matter (DOM), where we assume different rate constants for the second-order reaction between HOI and DOM (l22). The reaction is shown as green arrow in Fig. 1. Evidently, the proposed reaction can only be important for the formation of iodide if its rate can compete with that of other reactions that consume either HOI (especially its reaction with X^-) or I^- (its reaction with HOX or with ozone).

We assume that organic matter is emitted from the ocean (from the ocean's surface microlayer or via bubbles that have scavenged organic material while rising to the ocean's surface) as part of the seasalt aerosol during bubble bursting. The prescribed DOM flux from the ocean's surface into seasalt aerosol results in a molar DOM fraction of about 1% of the total aerosol (i.e., about 0.2 M near the ground). For
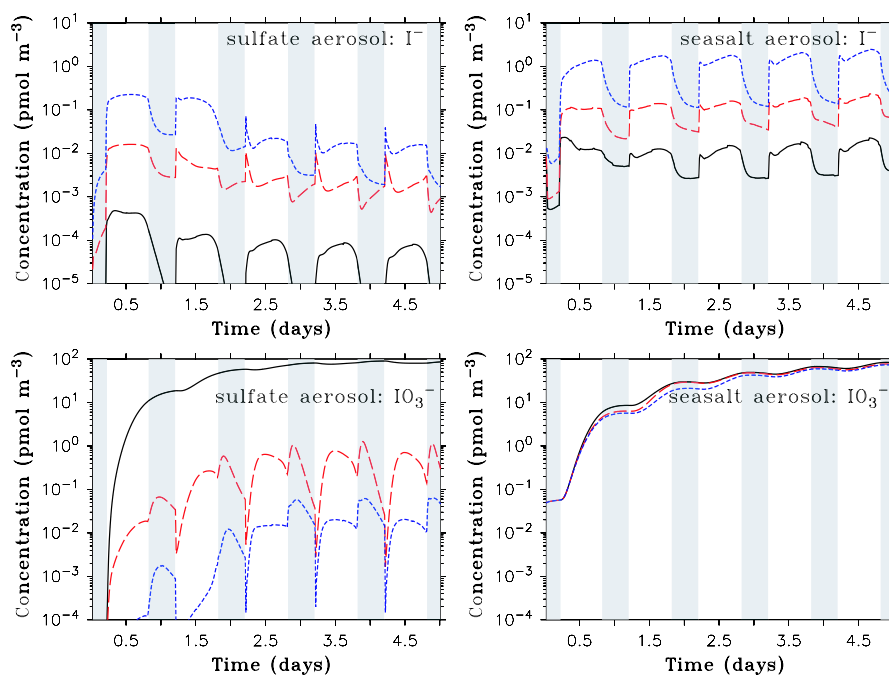
Fig. 6. 5-days timeseries of I^- and IO_3^- in 15 m altitude for BASE (black, solid) and ORG with a second order rate coefficient for the reaction between HOI and DOM of $10^5\,M^{-1}\,s^{-1}$ (red, dashed) or $10^7\,M^{-1}\,s^{-1}$ (blue, dotted). Note the logarithmic y-axis. Nighttime periods are grey-shaded.

the "sulfate" aerosol, we prescribe an initial DOM fraction of 10% (i.e., about 0.7 M near the ground). As the organic fraction in ambient aerosol is highly variable, these numbers chosen for the model's bulk aerosol are of course somewhat arbitrary, but the higher organic fraction in the fine aerosol mode (sulfate aerosol) compared to the coarse aerosol mode (seasalt aerosol) seems at least plausible. In both aerosol modes, the organic fractions stays approximately constant during the model simulations.

The reaction rate constant for the second-order reaction rate of HOI with DOM was set to either $10^5\,M^{-1}\,s^{-1}$ or $10^7\,M^{-1}\,s^{-1}$. These values were chosen such that the reaction can compete with other reactions consuming HOI, although they seem rather high compared to rate constants determined by Truesdale et al. (1995a,b) for the reaction of "apparent iodine" (mainly I_2 and HOI) with organic reducers in seawater: For different seawater samples, Truesdale et al.'s rate constants vary from about $1 \times 10^2\,M^{-1}\,s^{-1}$ to $5.2 \times 10^4\,M^{-1}\,s^{-1}$. However, considering this large variability even within different seawater samples, higher rate constants within aerosol samples appear to be possible. Specific laboratory investigations are urgently needed.

In this context it should also be mentioned that the choice of the rate constant and the choice of the DOM fraction in aerosol are not completely independent: For higher DOM fractions, the same effect (in terms of reaction rates) would be gained already for smaller rate constants and vice versa.

In Fig. 6 we compare 5-days timeseries of the BASE simulation with the ORG simulation, where DOM has been introduced as just described. Including the reaction of HOI with DOM increases I^- by about 2 to 3 orders of magnitude compared to BASE for both sulfate and seasalt aerosol, leading to iodide concentrations of up to about 0.3 pmol m^{-3} for sulfate and about 3 pmol m^{-3} for seasalt, which is well within the range measured by Baker (2005).

Besides this direct production of I^- by the reaction of HOI with DOM, there are also indirect consequences that result from the increase of the I^- and the decrease of the HOI concentrations. Most importantly for the scope of our paper is that enhanced I^- leads to a general increase in the reaction rates of (I19−) and (I20−), and thus to a greater potential for IO_3^- reduction. Furthermore, there is also a shift in the relative importance of these two reactions: While for the low iodide concentrations of BASE, (I19−) dominates over (I20−), the significantly higher iodide concentrations of DOM lead to the dominance of (I20−), whose reaction rate has a quadratic dependence on $[I^-]$. In case of the low-pH sulfate aerosol, IO_3^- concentrations decrease by as much as 2 to 3 orders of magnitude from maximum values of about 80 pmol m^{-3} (in BASE) to about 1 pmol m^{-3} or even 0.07 pmol m^{-3} (in ORG, red and blue lines in Fig. 6), i.e., values that are at or below the detection limit of the instrumentation used by Baker (2005). Therefore, it seems that the reaction of HOI with organic material could not only efficiently produce iodide, but

could at the same time induce an efficient reduction of iodate, at least for acidic aerosol.

For the less acidic seasalt aerosol, the reduction of iodate due to enhancement of I$^-$ is much smaller due to the still much smaller reaction rates of (I19−) and (I20−) (which is due to the much lower [H$^+$]): IO$_3^-$ values decrease only slightly by up to $10 \, \mathrm{pmol} \, \mathrm{m}^{-3}$. Even this slight decrease is not only an effect of iodate reduction by (I19−) and (I20−), but also an indirect effect of the lower HOI concentrations: Lower liquid-phase HOI leads to less production of IX (except for I$_2$ whose production is enhanced due to larger I$^-$ concentrations), less release of these species to the gas phase and, via the whole gas phase reaction mechanism, to a slightly decreased production of HIO$_3$, which is the main gas phase precursor of IO$_3^-$.

For the reasons just explained, gas phase mixing ratios of ICl and IBr decrease if the reaction of HOI with DOM is included in the model simulations, while gas phase mixing ratios of I$_2$ increase from maximum values of about $0.1 \, \mathrm{pmol} \, \mathrm{mol}^{-1}$ (in BASE or OLD) to about $0.5 \, \mathrm{pmol} \, \mathrm{mol}^{-1}$ (in DOM). In the gas phase, photolysis of IX followed by the reaction of the generated I radicals with ozone leads to the formation of IO which can further react to OIO (for details in the gas phase chemical mechanism see Pechtl et al., 2006), i.e., changes in aqueous phase chemical reactions potentially affect mixing ratios of most gas phase iodine compounds. However, the model simulations show only negligible changes in IO and OIO mixing ratios with and without the reaction of HOI with DOM. Thus, from our model results it seems unlikely that discrepancies between measured and modelled iodine oxide concentrations are mainly due to deficiencies in aqueous phase iodine chemistry. For coastal regions, where the emissions of iodine precursor compounds from algae etc. tend to be much stronger than over the open ocean, the importance of recycling processes from the aqueous phase for gas phase iodine mixing ratios is probably even smaller.

As explained above, the different effects on iodate concentrations in sulfate and seasalt aerosol in the model depends mostly on the different pH values. Convincing observational evidence for this finding is still missing, but the measurements of Baker (2005) do at least give a hint that this might be realistic: Baker (2005) found iodate enriched predominantly in his coarse aerosol mode (d>1 μm), while the fine mode (d<1 μm) often contained very little amounts of iodate. Assuming that the collected coarse particle fraction contains more (fresh) seasalt than the fine particle fraction, it is very likely that the pH of that fraction indeed tends to be higher, leading (according to our chemical mechanism) to a less efficient iodate reduction. Another evidence for the importance of aerosol pH is Baker's finding that the highest measured iodate concentrations coincide with the occurrence of alkaline Saharan dust (A. R. Baker, personal communication).

For a reasonable agreement of the model results with the iodide concentrations measured by Baker (2005), the reaction rate coefficient for the reaction of HOI with DOM has to be at least about $10^5 \, \mathrm{M}^{-1} \, \mathrm{s}^{-1}$. Otherwise, the reaction does not have the potential to modify the chemical cycles strongly enough. Laboratory studies that investigate the reaction of HOI with different kinds of organic material, as well as studies on organic iodine chemistry in general are urgently needed in order to test the significance of organic iodine chemistry for the speciation of iodine and iodate in aerosol.

4 Conclusions

Using an updated aqueous phase iodine chemistry mechanism, our model studies have shown that the transformation of particulate iodide to volatile iodine species likely has been overestimated in earlier studies, especially for acidic aerosol. Furthermore, we showed that, unlike previously assumed, iodate can be reduced in acidic media by inorganic reactions, leading to a better agreement between modelled and observed iodide and iodate concentrations. However, even for the updated inorganic chemical mechanism the modelled aerosol iodide concentrations are still significantly lower than observed values.

An efficient increase in iodide concentrations could be caused by organic iodine chemistry. According to our model studies, the reaction of HOI with dissolved organic matter can efficiently enhance iodide concentrations if the reaction is fast enough to compete with reactions of the inorganic cycle. As an indirect effect of the enhanced iodide concentrations, that reaction also triggers a speed-up of the inorganic iodate reduction that could even result in near-zero iodate concentrations in strongly acidic aerosol.

Our finding that the efficiency of iodate reduction significantly increases with decreasing pH of the aerosol is indirectly supported by the observations of Baker (2005), who found iodate depleted especially in the fine aerosol mode (which is likely to have lower pH-values than the coarse mode due to a smaller seasalt fraction) and the highest iodate concentrations in the presence of alkaline Saharan dust.

Of course, our studies are somewhat idealized with only two types of aerosol, each with a uniform pH-value for the whole aerosol mode. However, our studies illustrated the significantly different behavior of aqueous phase reaction cycles at differing pH, for example iodate reduction, ranging from a nearly complete loss of iodate in very acidic aerosol (pH about 0.5) to nearly no iodate reduction in near-neutral aerosol (pH about 6). In reality, each aerosol particle is an individual "chemical laboratory" with unique properties that may change continuously during its lifetime. The strong pH dependence of both iodate reduction and iodide oxidation may offer an explanation for the large variability of

concentrations that were found during the measurements of Baker (2005).

The aqueous phase chemistry is strongly coupled to the gas phase via exchange processes of different iodine species to and from the aerosol. Gas phase HI and HIO_3 are the strongest sources for aerosol iodide and iodate content, i.e., their gas phase mixing ratios significantly affect the aqueous phase. Of course, their amounts do not only depend on the whole set of chemical reactions occurring in the gas phase, but also on the strength of iodine sources (e.g. open ocean versus coastal regions) as well as on ambient concentrations of other trace gases such as NO_x. Thus, a large variability is possible regarding the source of aerosol iodide and iodate, offering a further explanation for their observed variability.

The changes in aqueous phase iodine chemistry feed back to the gas phase via exchange processes. According to our model simulations, gas phase mixing ratios of I_2 tend to increase if the reaction of HOI with DOM is included, while the effect on IO and OIO is negligible. In conclusion, on a larger scale one would expect a substantial variability of both gas phase and aqueous phase iodine dependent mainly on the source strength of iodine precursor compounds, and an additional substantial variability of the aerosol iodide and iodate contents dependent on the presence of dissolved organic matter within the aerosol particles.

Although the present paper has suggested a mechanism how to diminish the disagreement between measured and modelled iodide and iodate contents in atmospheric aerosols, many uncertainties and open questions still remain. First, aqueous phase iodine chemistry is far from being completely understood, even regarding inorganic chemistry: This refers to uncertain reaction rates, possibly unknown inter-halogen reactions or reactions of iodine compounds with other dissolved species. Second, the formation of gas phase HIO_3, the most important precursor of aerosol iodate, is quite uncertain, both regarding its formation pathways and the respective reactions rates. Third, the current knowledge about atmospheric organic iodine chemistry is poor, very little qualitative and almost no quantitative information is available yet. The existence of organic forms of iodine as inferred by Baker (2005) has to be reconfirmed in further measurements and its consequences for chemistry in general and iodine speciation in particular have to be investigated. In this context, also the fate of freshly nucleated iodine particles would be interesting as these could, if growing or being taken up by other particles also affect iodine speciation in atmospheric aerosol.

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