Box modelling of gas-phase atmospheric iodine chemical reactivity in case of a nuclear accident

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Abstract

A new atmospheric iodine gas-phase mechanism containing 248 reactions combined to the RACM air quality mechanism was implemented into a 0D box model in order to evaluate the behaviour of iodine fission products released in the atmosphere. Different simulation scenarios were performed unravelling the influence of several parameters on the iodine speciation (season, day/night, low/medium/high iodine concentration release, nature of the injected iodine species). The main outcomes of our work are the following: (i) the I₂ reactivity is faster than that of CH₃I, (ii) iodine nitroxides INO_x are mainly formed during night with low and medium releases in winter, (iii) iodine oxides are promoted with a high release of I₂ during summer, (iv) the formation of organic iodine compounds can be highlighted only in the case of a low I₂ release. In this work, I₂O, I₂O₅, and HOIO₂ are the most abundant iodine oxides because their atmospheric removal pathways in the gas-phase are not yet known. The main iodinated organic species is CH₃OOI arising from the reaction between I atom and the methyl peroxy radical. In case of a CH₃I release, before the I atom formation, the reaction mechanism leads to either the formation or the destruction of several other organic iodinated compounds such as CH₂IOH and CH₂IOO.

Keywords: Iodine; atmosphere; nuclear safety; 0D modelling

1. Introduction

Interest in iodine atmospheric chemistry is widely focused on the Marine Boundary Layer (MBL) where are localized principal natural sources of molecular iodine (I_2) and iodocarbons (RI) such as CH_3I and CH_2I_2 emitted by macro algae and phytoplankton (Saiz-Lopez et al., 2006; von Glasow and Crutzen, 2003). Measurements conducted at Mace Head Research Station (Ireland) of the reactive iodine species (IO, OIO, CH_3I , and I_2) detected mixing ratios around the pptV level reaching 100 pptV for the "hot-spots" (Seitz et al., 2010). The residence time of iodine species in the atmosphere is ranging from few days (CH_3I) to seconds (I_2), it is linked directly to the solar photolysis level but it should be increased by formation of particles (McFiggans et al., 2004). Iodine species could affect the trace gas composition of the atmosphere by reaction with primary and secondary pollutants. Their impacts on ozone cycle and NO_x regimes (Saiz-Lopez et al., 2014; Saiz-Lopez et al., 2012) or tropospheric HOx (OH and HO_2) (Stone et al., 2018; Stone et al., 2012) have been significantly studied. Models are usually used to predict the impacts and behaviour of such species in the MBL or for global scale (Sherwen et al., 2016b) and various iodine chemistry schemes were developed and evaluated by comparison between field measurements and modelling (Sommariva et al., 2012).

Our work takes place in the field of the chemistry and transport modelling of fission products following a severe nuclear accident to predict the radiological consequences on the populations. Among fission products, iodine-131 whose half-life is equal to 8 days, is recognized as the main radionuclide due to its ability to accumulate in the thyroid gland, thereby increasing the effects of radiation on the human body. After the Fukushima accident, dispersion tools have been used and simulation results compared to measurement highlighted significant underestimating of the iodine radiation levels at the ground (Korsakissok et al., 2013). These differences could be explained by the fact that modelling tools used does not consider chemical transformations during transport in the atmosphere. The capture of gas-phase species by atmospheric particles and the aerosol formation processes (nucleation, coagulation, ...) imply an increase of the radioactive deposition. It is very important to take into account the atmospheric iodine reactivity. For this purpose, we developed an exhaustive iodine gas-phase chemical mechanism, which is then combined to the air quality Regional Atmospheric Chemistry Mechanism (RACM) (Stockwell et al., 1997) and implemented on a

0D box-model. The aim is to explore the variation of atmospheric concentrations and speciation of iodine modelled for various source term configuration (concentration and speciation, CH_3I , I_2 , I_2O_5) with realistic ambient conditions.

This paper is organized as follows. Section 2 described the methodology used to develop the gas-phase iodine mechanism as well as the 0D model for the evaluation of iodine reactivity as a function of various atmospheric conditions (photolysis conditions, night or day, winter or summer) and source term values. In section 3, the simulation set-up and input data is presented while section 4 contains the results and discussion.

2. Iodine mechanism and 0D model presentation

2.1. Iodine gas-phase mechanism

Several 0D or 3D modelling studies have already used an iodine gas-phase mechanism (Furneaux et al., 2010; Mahajan et al., 2009; McFiggans et al., 2000; Ordóñez et al., 2012; Pechtl et al., 2006; Saiz-Lopez et al., 2016; Saiz-Lopez et al., 2008; Sherwen et al., 2016a; Sherwen et al., 2016b; Sommariva et al., 2012). Table 1 lists the main informations about the number of organic and inorganic reactions involving the gas-phase iodine-containing species reactivity (thermal and photolysis). These mechanisms do not consider any organic reactivity and the extent of inorganic mechanism is variable.

The strategy used to constitute the reactional mechanism was to collect all gas-phase reactions involving iodine-containing species through the literature for a wide range of temperature from atmospheric to nuclear accident conditions (213 - 2500 K). The mechanism does not contain reactions involving other halogen atoms such as chlorine and bromine. The elaboration of the mechanism has been done using the most recent evaluations available arising from the National Institute of Standards and Technology (NIST) kinetic database (Manion et al., 2015), International Union of Pure and Applied Chemistry (IUPAC), and Jet Propulsion Laboratory (JPL) evaluations (Burkholder et al., 2015).

For most of reactions, there is a good agreement with the recommended values of the thermokinetic parameters between the different databases. If it's not the case, the selected values correspond to the most recent experimental data. When reactions are missing, an examination of the theoretical works available in the literature (Bai et al., 2015; Canneaux et al., 2010; Cours et al., 2013; Fortin et al., 2018; Gómez Martin et al., 2013; Hammaecher et

al., 2011; Kaltsoyannis and Plane, 2008; Khanniche et al., 2016b; Louis et al., 2011; Plane et al., 2006; Saiz-Lopez et al., 2016; Xerri et al., 2012) was performed and the corresponding thermokinetic data was added to the mechanism.

For an overall reaction involving several reaction pathways, the following procedure has been applied: i) select experimental data, ii) if branching ratios were not determined experimentally, select theoretical values if available. For example, in the case of the self-reaction of IO (R76, A. 2 for reaction number 76 in Appendix 2), the overall rate constant was taken from the work of Atkinson et al. (Atkinson et al., 2007) while the branching ratios were taken from the estimation made by Gómez-Martin et al. (Gómez Martín et al., 2007) for the four reaction pathways leading to $I_2 + O_2$, $2 I + O_2$, $I + OIO$, or I_2O_2 .

The iodine gas-phase mechanism does not include reactions for which the thermokinetic data were assimilated to those of other halogen atoms. These estimations generated too much uncertainties to be taken into account. It was recently demonstrated for the reactions of halogen atoms with hydrogen peroxide (Fortin et al., 2018). A strong influence of the nature of the halogen atom on the rate constant at 298 K was shown with a change in the values of about twelve orders of magnitude when going from chlorine to iodine.

The updated iodine gas-phase mechanism contains 231 reactions (139 and 92 for organic and inorganic species), 17 photolysis reactions (6 and 11 for organic and inorganic species). This mechanism is presented in Appendices A1-A4 with the corresponding references for each reaction. It is then combined to the air quality RACM mechanism (Stockwell et al., 1997), which contains 237 reactions (23 photolysis reactions) involving 77 species. The aggregation procedure developed for organic iodine species is the same as RACM mechanism organic section (see IRACM class in Table 2 and corresponding IRACM reactions in Appendices A1 and A3).

2.2. Model presentation

The iodine mechanism described in previous section has been implemented in the ASTEC (Accident Source Term Evaluation Code) software dedicated to model a nuclear severe accident (Chatelard et al., 2016), which was developed by the French Nuclear Safety Institute (IRSN). It is divided into several modules taking into account each possible phenomenon that can occur during the accident. Iodine is the main important radio-element due to its radio-toxicity. Therefore, iodine chemistry is an important process, which has to be

modelled during a severe accident. A dedicated module called SOPHAEROS (Cousin et al., 2013) is implemented in the ASTEC code to model the iodine chemistry.

The SOPHAEROS module used a 0D approach to compute iodine chemistry. The implementation of iodine mechanism in SOPHAEROS has to be sufficiently flexible due to on-going researches on iodine behaviour during a severe accident (Bosland et al., 2010; Cantrel et al., 2014; Girault et al., 2012). The 0D box model is defined with a fixed volume. The inside conditions are characterized by different parameters: temperature, pressure, volatile organic compounds (VOC) and NO_x emissions. The model computes the mass evolution solving a differential equation for each species involved in the mechanism using a Newton-Raphson algorithm.

3. Input data and Simulation set-up

3.1. Air quality conditions

All simulations were made at constant atmospheric temperature (298 K) and pressure (1.013 bar). The box volume is fixed to 10000 m³. To take into account the reactivity of iodine with atmospheric species, initial ambient concentrations were fixed for H₂, H₂O, H₂O₂, OH, HO₂, N₂, and O₂ (see Table 3 and corresponding references therein). We modelled the temporal variation of NO_x and Volatile Organic Compounds (VOC) emissions based on Kuhn et al. values (Kuhn et al., 1998) given in Table 4 and Menut et al. temporal profile (Menut et al., 2013). The 67 VOC species proposed by Kuhn et al. (Kuhn et al., 1998) were aggregated into the RACM VOC chemical scheme whose obtained speciation is given in Table 5. Iodine release was made after a spin-up time necessary to achieve O₃ and VOC/NO_x realistic conditions (from 12 to 24 hours depending on the scenario season). Network station measurements in the North of France (15 stations) were chosen as reference for O₃ concentration, NO_x speciation (NO: 98%, NO₂: 2%), and VOC/NO_x ratio. The ozone concentration values range between 1 and 92 µg m⁻³ while the VOC/NO_x ratio vary from 3 to 10. Both depends on month and time of the day.

For photolysis rates, actinic flux was calculated with the Tropospheric Ultraviolet and Visible (TUV) radiation model, which was available from the National Center for Atmospheric Research (NCAR) for clear sky, beginning of January and August, latitude 51° 2' 3,725"N and longitude 2° 22' 36,394" E. The cross sections and quantum yields used are detailed in Appendices A3-A4 for organic and inorganic species, respectively.

3.2. Iodine speciation and amount

During the Chernobyl accident, it was estimated around 1760 PBq of ^{131}I isotope released to environment (IAEA, 2006), which corresponds to 380 g of ^{131}I . Because the ^{131}I isotope is a small fraction of total iodine isotope inventory, it can be estimated that few kilograms of stable and radioactive iodine isotopes were released.

In the same way, during the Fukushima accident, (Katata et al., 2015) or (Lebel et al., 2016) estimated around 160 PBq of I^{131} isotope released. Saunier and co-workers (Saunier et al., 2013) made a lower evaluation around 100 PBq. It corresponds to a value varying between 20 and 30 g of ^{131}I isotope. The global Fukushima release can be estimated around 1 or 2 kg of stable and radioactive iodine isotopes. One can notice that at the source level the nuclear release infers higher mass of iodine than in natural marine conditions (Saiz-Lopez et al., 2012).

Obviously, the main parameter for iodine chemistry in the atmosphere is not the total amount of iodine, which can be released during an accident but the initial iodine concentration and speciation in the puff during the release. This speciation and concentration are not easy to define near the nuclear power plant. Iodine speciation in the containment depends on several parameters such as temperature, water, and gaseous dose rate, sump pH, organic compounds (Cantrel et al., 2014; Girault et al., 2012). The speciation is governed by the competition between the iodine formation/desorption and destruction/adsorption processes that take place in the atmosphere of the containment and in the water. The main iodine species formed are inorganic iodine considered as molecular iodine, organic iodine represented by the most volatile one, the iodomethane CH_3I and iodine oxide. With these three kind of species, taking into account several radiolytic and thermal reactions, it is possible in a severe accident code to model integral experiments such as ones from the Phebus FP (Fission Product) Program (Girault et al., 2012). The iodine oxides are known to nucleate and form particles (Hoffmann et al., 2001; Saunders and Plane, 2006). That's why they are considered as aerosols in the atmosphere of the nuclear power plant.

The repartition of these three species is not constant during the accident. To cover all the initial speciation, which can be released in the environment, it is necessary to consider a mix of organic, inorganic, and iodine oxide in the puff. To define representative iodine concentration during the release, it is necessary to estimate the fission product behaviour during a severe accident from the release from fuel pellets to the release in the environment. This behaviour is directly dependent on thermal-hydraulics conditions in the nuclear power plant, leakage to environment, fission product transport, and chemistry.

The aim of the ASTEC code is to model all these phenomena to give an assessment of the global release called source term. A lot of uncertainties have to be considered in this source term evaluation. (Chevalier-Jabet et al., 2014) studied the source term uncertainties regarding iodine chemistry mechanism in the containment with the ASTEC code on a severe accident transient on a Pressurized Water Reactor (PWR) of 1300 MWe. In the containment, the iodine mass can vary between 10^{-5} to 10^{-10} kg, which corresponds to 10^{-4} to 10^{-10} kg m⁻³ assuming a reactor building volume around 80000 m³. In a nuclear power plant, several aerosol and gas filters are used to reduce the release during the accident. Regarding the physical form of iodine (aerosol, gaseous molecular iodine, gaseous organic iodine), filter efficiency can vary a lot. A good decontamination factor can be estimated around 1000 whereas a poor decontamination factor is around 10. If these values are applied to iodine concentration in the containment, the iodine quantity released in the atmosphere during an accident can be evaluated between 10^{-5} to 10^{-13} kg m⁻³. This range of concentration can be reduced if it is assumed high efficiency of the filter for aerosol. This form of iodine is predominant at the beginning of the release (Chevalier-Jabet et al., 2014), which leads to a maximal level around 10^{-7} kg m⁻³. At long term, after aerosol deposition, iodine in the atmosphere is due to gaseous chemistry and compounds transferred from water to gas phase (Girault et al., 2012). Iodine gaseous species are more difficult to trap but this low efficiency can be applied to lower concentration. It leads to a minimal level around 10^{-11} kg m⁻³. Iodine source term was injected in the box during one second with mass flow rates 10^{-7} to 10^{-11} kg m⁻³ s⁻¹.

3.3. Model scenarios

We considered various representative scenarios as described in Table 6. Parameters studied are high (H), medium (M), and low (L) levels for source term quantity (10^{-7} , 10^{-9} , and 10^{-11} kg m⁻³, respectively), I₂ or CH₃I iodine speciation, nightly (N) or daily (D) release, and month of the year, January for winter (W) or August for summer (S). In the model, source term concentrations are given in pptV. For example, a medium release value (10^{-9} kg m⁻³) corresponds to either 98 pptV for I₂ or 196 pptV for CH₃I.

4. Results and discussion

Iodinated compounds are grouped into five families: iodine nitroxides INO_x (INO, INO_2 , $IONO_2$), iodine organic species I_ORG . (molecules and radicals), iodine oxides I_xO_y (I_2O , I_2O_2 , I_2O_3 , I_2O_4 , I_2O_5 , and its hydrated form $HOIO_2$), inorganic iodine species I_INORG . (I_2 , HI, HOI), and iodine radicals R_INORG . (I, IO, OIO).

4.1. Iodine nitroxides formation

4.1.1. Iodine nitroxides regarding I_2 or CH_3I release

Figure 1 displays the temporal iodine speciation obtained with January photolysis conditions for low, medium, and high daily I_2 or CH_3I release. The INO_x family is more important and faster produced with an I_2 release. At midnight, 17 hours after the release, 97 % of iodine nitroxides are formed with an I_2 release of 0.98 pptV (Fig. 1 (a)) compared to only 21 % with the CH_3I release of 1.96 pptV (Fig. 1 (b)). The iodine species released have an important impact on the iodine nitroxides formation rate. For example, 14 hours are needed for CH_3I release to reach the same level of iodine nitroxides (20 %) reached in one hour with an I_2 release (Fig. 1 (a) and (b)). The same evolution is noticed for simulations with medium release (Fig. 1 (c) and (d)).

The delay to obtain INO_x compounds with the CH_3I release can be explained regarding the kinetic scheme presented in Fig. 2. The I_2 photolysis is faster by comparison to that of CH_3I . As seen in Appendices 3 and 4, the I_2 photolysis rate constant J is about 10000 times greater than the one of CH_3I . It can be also noticed that more reaction steps are needed in the case of the CH_3I release:

compared to the I_2 release:

For the CH_3I release, iodoalkanes and CH_2IOH are treated as I_HC3 species in the IRACM aggregation scheme. The atmospheric degradation of iodomethanol can be considered by analogy to another iodinated alkane compound. Similar reactions can be expected and are represented by dashed red lines in the Fig. 2 (b). For example, the CH_2IOH photolysis is expected to be close to that of an iodinated propane $\text{C}_3\text{H}_7\text{I}$, which belongs to the same I_HC3 family.

In case of an high release (Fig. 1 (e) and (f)), the iodine concentration in the box is greater than the concentration of atmospheric pollutants (O_3 , NO_x). These pollutants are quickly consumed to form INO_x and I_xO_y species. Their quantity depends only on the O_3 and NO_x concentrations. After 24 hours, about 85% of iodine release remains in the simulation. To get a more precise behaviour with high release conditions, the use of a Chemical Transport Model (CTM) or Puff model is needed.

4.1.2. Iodine nitroxides speciation

Fig. 3 presents the temporal INO_2 and IONO_2 mass speciation for the different scenarios. Nitrosyl Iodide (INO) is not represented on the Fig. 3 because its speciation is less than 0.01% of the total INO_x . Regardless of the nature of the injected iodinated compound (I_2 or CH_3I), iodine nitrate (IONO_2) is the main INO_x species formed (around 99.9%) for low and medium releases (Fig. 3 (a), (b), (c), and (d)). The INO_2 species is produced during the day and can represent up to 5% of the total INO_x (Fig. 3 (c)). A day/night cycle appears for both species. This cycle is more significant in the case of high releases (Fig. 3 (e) and (f)).

Fig. 4 presents the iodine reaction scheme for an release of 98 pptV of I_2 during day (Fig. 4 (a)) and night (Fig. 4 (b)) in January.

During the night, main reactions are driven by the nitrate radical (NO_3). IONO_2 is mainly formed by the following reaction

During the day, the photolysis reaction of iodine nitrate

leads to the IONO_2 destruction. The formation of INO_2 by the reaction

can be significant within the INO_x family.

Since the day/night cycle has an impact on the iodine nitroxide formation, obviously, the month of release will affect the INO_x reactivity. Fig. 5 displays the family evolution of iodine for a medium release of I_2 during day and night in winter and summer. It can be noted that, independently of the season release, there is a rapid formation of nitroxide species during the day. Afterwards, their destruction occurs due to photolysis reactions. Obviously, photolysis reactions are more efficient in summer, which leads finally to a lower amount of iodine nitroxide species 22% in summer after 24 hours (Fig. 5 (c)) compared to winter 96% (Fig. 5 (a)). During night, the season does not affect strongly the INO_x formation. Reactive schemes obtained for summer test cases are very similar to those of winter presented in Fig. 4.

4.2. Iodine oxides formation

4.2.1. Iodine oxides regarding I_2 or CH_3I release

Fig. 6 presents the family mass evolution of iodine in the case of I_2 and CH_3I medium release at 4 am in August. At noon, 8 hours after release, I_xO_y family represents 74% of the total iodine compared to 4% in case of the CH_3I release. The iodine oxide formation raises as the iodine injected quantity increases for low and medium release scenarios (I_2 or CH_3I). It is worth noticing that iodine oxide species are not present in such quantities in winter with low and medium releases ($< 1\%$). The iodine reaction scheme corresponding to the previous simulation scenario is depicted in Fig. 7 for I_2 (a) and CH_3I releases (b). As already discussed in the iodine nitroxides formation (see 4.1.1.), more reaction steps are needed to get the key precursor species of iodine oxides ($R_INORG.$) with the CH_3I release.

I_2O_3 is considered as one of the gas-phase main precursor of higher iodine oxides species, his formation is obtained by either the biradicalar reaction

or the I_2O_2 oxidation by ozone

In the CH_3I release scenario, only the reaction of iodine monoxide with iodine dioxide (R83, A.2) is significant.

4.2.2. Iodine oxides speciation

Fig. 8 presents the iodine oxides speciation corresponding to the evolution and simulation conditions presented in Fig. 6. Regardless of the nature of the injected iodine (I_2 or CH_3I), the same iodine oxides species are formed. The major species are I_2O , I_2O_5 , and the iodic acid $HOIO_2$ while I_2O_2 , I_2O_3 , and I_2O_4 are present in less quantities. These latter act as

intermediate compounds leading to the formation of gas-phase I_2O_5 and HOIO_2 . To the best of our knowledge, there are no literature data concerning the atmospheric fate of I_2O by photolysis or reactions with other iodine oxides. Its removal from the atmosphere is only assessed by the reaction with I atoms

These facts can explain the high level of I_2O concentrations found in our simulations.

The comparison between low, medium, and high I_2 release highlights the increase of I_2O formation by the reaction

In the high concentration scenario, there are two distinct reaction paths explaining the formation of major iodine oxide species

path I:

path II:

followed by the same final reaction scheme:

The atmospheric removal of iodine pentoxide and its hydrated form HOIO_2 is not well evaluated in the literature with the exception of the reaction of OH radicals with iodic acid for which a recent theoretical study was performed in our group (Khanniche et al., 2017) enabling to get the kinetic parameters over a wide temperature range (250 - 2500 K). This work showed that the H-abstraction pathway was the most important and the value of the rate constant at 298 K was about $10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. It was concluded that HOIO_2 could be transported to different places around the Earth. Recent field measurements in various locations confirmed the presence of iodic acid (Kürten et al., 2016; Rissanen et al., 2019; Sipilä et al., 2016).

Other atmospheric removal reactions of I_2O_5 or $HOIO_2$ such as nucleation or condensation onto aerosols have to be taken into account (Hoffmann et al., 2001; Saiz-Lopez et al., 2012; Sipilä et al., 2016) when using a multiphase modelling approach.

4.2.3. Photolysis impact on iodine oxides formation

Iodine oxides are produced faster in summer than in winter. At noon, 20% of iodine corresponds to iodine oxides in winter (see WDM- I_2 scenario, Fig. 5 (a)) while this proportion reaches about 60% in summer (see SDM- I_2 scenario, Fig. 5 (c)). Similar trends are found when injecting organic iodine. These remarks can be attributed to both photolysis conditions and ozone production with an average value varying from 30 to 50 $\mu\text{g m}^{-3}$ in winter and summer, respectively.

There is no impact of the season release on the iodine oxides speciation. Same major species are found (I_2O , I_2O_5 and $HOIO_2$).

4.3. Organic iodine

4.3.1. Organic iodine formation with I_2 release

In order to evaluate the interaction between iodine and atmospheric VOC, we study the scenario of an I_2 release as depicted in the Fig.1 at 7 am in January. In the case of the WDH- I_2 scenario (high release of I_2), the formation of organic iodine species is found negligible while it can reach a few % in the WDL- I_2 scenario (low release of I_2). These trends are also true for an release during summer conditions. Regarding speciation, there is a mix of CH_3OOI and other unknown organic compounds. It can be viewed on Fig. 2 (a), Fig. 4 (a), and Fig. 7 (a) that CH_3OOI is obtained by the following reaction

The methylperoxy radicals arise from the atmospheric VOC oxidation. The interaction of iodine with VOC in the atmosphere is therefore not negligible especially during summer when iodinated organic products formed can reach 10% of the total iodine mass.

There is only one reaction consuming the CH_3OOI species

The unknown organic compounds come from reactions experimentally observed without determination of all the products and the corresponding branching ratios (noted as "products" in the reaction mechanism). These species will be therefore accumulated. It is the case for example of the following reaction:

The examination of literature data exhibits at least 10 different reaction channels (Bale et al., 2005; Dillon et al., 2006; Drougas and Kosmas, 2007; Enami et al., 2006)

Previous modelling studies (Saiz-Lopez et al., 2016; Sommariva et al., 2012) only consider the formation of I, HO₂, and HCH(O) (R33 path VI). This biradicalar reaction is also complex to be treated from a theoretical point of view as it involves two different potential energy surfaces (singlet and triplet), the presence of different adducts (CH₃OOIO, CH₃OOOI) and their atmospheric decomposition pathways.

4.3.2. Organic iodine formation with CH₃I release

Fig. 9 presents the organic iodine evolution repartition with CH₃I release at 7 am in January. CH₃I represents 10% of organic iodine species after 13 hours for a low release compared to 15 hours for a medium release. Three other organic species are produced (CH₂IOH, CH₂IOO, and CH₃OOI). Higher is the concentration release, higher is the CH₂IOH production compared to CH₂IOO and CH₃OOI. Similar trends are observed for release in summer and during night. The reaction mechanism leads to several intermediate organic iodine species before reaching the inorganic reaction scheme with the I atoms (see Fig. 2 (b)).

4.4. Day/night cycle impact

Previous analyses showed that iodine reactivity is totally different during day and night. Fig. 10 (a) and (b) presents a reactive scheme for an I₂ release during day and night in summer.

During daytime, main reactions are driven by photolysis. I_2 is mainly dissociated by photolysis to form I radical

Photolysis reaction has also an impact on the iodine nitrate destruction

During the night, the iodine reactivity is driven by the nitrate radical. Its chemistry with iodinated species is not well known nowadays. The main reaction leads to the $IONO_2$ formation

4.5. Influence of the added reactions to the iodine mechanism

A comparison was made with the most recent mechanism proposed by Saiz-Lopez and co-workers (Saiz-Lopez et al., 2016) (see Table 1) for two scenarios simulations (SDM- I_2 and WDM- I_2). The results are shown in the figures 11-12. The $I_INORG.$ family (mostly I_2) is more rapidly consumed with our mechanism. As a consequence, we observe a more important I_xO_y formation (especially for the SDM- I_2 scenario). This behaviour can be attributed by the fact that in our mechanism we consider all I_xO_y nucleation reactions as well as the chain reactions of I_2O_3 and I_2O_4 with O_3 leading to the I_2O_5 formation.

5. Conclusion

A new gas-phase iodine mechanism containing 248 reactions combined to the RACM air quality mechanism was implemented into the ASTEC 0D model in order to evaluate the behaviour of iodine fission products in the atmosphere. Different simulation scenarios carried out highlighted that I_2 and CH_3I can react with ambient pollutants like O_3 , NO_x , or VOC to form iodine nitroxides, iodine oxides, and other organic and inorganic iodinated species. The I_2 reactivity is faster than that of CH_3I and impacts the formation of other species.

Iodine nitroxides are mainly formed during night with low and medium releases in winter. Iodine nitrate is the main iodine nitroxide formed during night while INO_2 can be formed during day especially if the I_2 concentration increases.

Iodine oxides are promoted with a high release of I_2 during summer. This is due to a strong relationship between iodine oxides formation and ozone concentrations. In this work, I_2O , I_2O_5 , and $HOIO_2$ are the most abundant iodine oxides because their atmospheric removal

pathways in the gas-phase are not yet known. The formation of organic iodine compounds can be highlighted in the case of a low I_2 release. The main species will be CH_3OOI , which is produced by the reaction between I atom and the methyl peroxy radical. In case of a CH_3I release, before producing the I atom, the reaction mechanism leads to either the formation or the destruction of several other organic iodinated compounds such as CH_2IOH and CH_2IOO . Iodine organic reactivity should be improved to get firm conclusions.

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Table 1

Gas-phase iodine mechanisms used in atmospheric modelling

# reactions	# Organic reactions	# Inorganic reactions	# Organic photolysis reactions	# Inorganic photolysis reactions	Model	Reference
23	1 ^a	13	3	6	0D	(McFiggans et al., 2000)
39	3 ^{a,b,c}	22	6	8	1D	(Pechtl et al., 2006)
36	1 ^a	27	3	5	1D	(Saiz-Lopez et al., 2008)
41	1 ^a	30	0	10	1D	(Mahajan et al., 2009)
45	1 ^a	33	3	8	0D	(Furneaux et al., 2010)
42	1 ^a	27	4	10	3D	(Ordóñez et al., 2012)
58	1 ^d	47	0	10	1D	(Sommariva et al., 2012)
59	3 ^{b,c,d}	40	4	12	1D/3D	(Saiz-Lopez et al., 2016)
43	1 ^a	28	4	10	3D	(Sherwen et al., 2016a; Sherwen et al., 2016b)

^a IO + CH₃SCH₃, ^b OH + CH₃I, ^c OH + C₃H₇I, ^d IO + CH₃O₂.

Table 2

IRACM organic class and organic iodine species associated

IRACM class	Species
I_ALD	CH ₃ C(O)I
I_CH4	CH ₃ I
I_CSL	iodobenzene
I_DIEN	iodocyclopentadiene
I_ETE	CH ₂ =CHI
I_ETH	CH ₃ CH ₂ I
I_ETHR	CH ₂ CH ₂ I, CH ₃ CHI
I_HC3	CH ₃ CHICH ₂ CH ₃ , CH ₂ ICH ₂ CH ₃ , t-C ₄ H ₉ I, s-C ₄ H ₉ I, n-C ₃ H ₇ I, i-C ₃ H ₇ I, t-C ₃ H ₇ I, CH ₃ CHICH ₃ , iodomethylcyclopropane, CH ₂ IOH
I_HC3R	CH ₂ CH ₂ CH ₂ I, CH ₃ CH ₂ CHI, CH ₃ CHCH ₂ I, CH ₂ CHICH ₃ , CH ₃ CICH ₃ , CH ₂ IO
I_HC5	Iodocyclopentane
I_HCHO	HC(O)I
I_MO2	CH ₂ IO ₂
I_MR	CH ₂ I
I_OLI	iodocyclopentene
I_OLT	CH ₂ =CHCH ₂ I
I_OP1	CH ₃ OOI
I_TOL	iodomethylbenzene
PROD	Products
I2_CH4	CH ₂ I ₂
I2_ETE	CHI=CHI
I2_ETH	CH ₂ ICH ₂ I, CH ₃ CHI ₂
I2_HC3	ICH ₂ CH ₂ CH ₂ I
I2_MR	CHI ₂
I3_CH4	CHI ₃

Table 3

Initial concentration in the box model

Species	Concentration (molecules cm ⁻³)	Reference
H ₂	1.34 × 10 ¹³	(Jacob, 1999)
H ₂ O	3.16 × 10 ¹⁷	(Jacob, 1999)
H ₂ O ₂	7.29 × 10 ⁹	(Acker et al., 2008)
OH	5.59 × 10 ⁶	(Stone et al., 2012)
HO ₂	5.59 × 10 ⁸	(Stone et al., 2012)
N ₂	1.95 × 10 ¹⁹	(Jacob, 1999)
O ₂	4.87 × 10 ¹⁸	(Jacob, 1999)

Table 4Emissions flux for NO_x and VOC

Emissions flux (molecule cm ⁻³ s ⁻¹)	
NO _x	1.1×10^6
VOC	3.0×10^6

Table 5

VOC speciation for the RACM mechanism

RACM species	Speciation %
ALD	0.53
ORA2	1.54
ETE	6.71
ETH	3.53
HC3	24.93
HC5	23.34
HC8	7.60
HCHO	2.04
KET	6.49
OLI	2.87
OLT	3.11
TOL	7.90
XYL	9.41

Table 6

Model scenarios

Parameter	Summer						Winter					
	Day-time scenarios			Night-time Scenarios			Day-time scenarios			Night-time Scenarios		
	Low	Medium	High	Low	Medium	High	Low	Medium	High	Low	Medium	High
	iodine	iodine	iodine	iodine	iodine	iodine	iodine	iodine	iodine	iodine	iodine	iodine
	SDL	SDM	SDH	SNL	SNM	SNH	WDL	WDM	WDH	WNL	WNM	WNH
I ₂ (pptV)	0.98	98	9800	0.98	98	9800	0.98	98	9800	0.98	98	9800
CH ₃ I (pptV)	1.96	196	19600	1.96	196	19600	1.96	196	19600	1.96	196	19600
Release												
Time (hour)	4	4	4	21	21	21	7	7	7	18	18	18

Figures

(a) WDL-I₂

(b) WDL-CH₃I

(c) WDM-I₂

(d) WDM-CH₃I

(e) WDH-I₂

(f) WDH-CH₃I

Fig. 1. Family mass evolution of iodine, 2013 January 1st, for an iodine release at 7 am with 0.98 pptV (a), 98 pptV (c), 9800 pptV (e) of I₂ and 1.96 pptV (b), 196 pptV (d), 19600 pptV (f) of CH₃I.

(a) WDL-I₂

(b) WDL-CH₃I

Fig. 2. Iodine reaction scheme, 2013 January 1st for iodine release at 7 am with 0.98 pptV of I₂ (a) and 1.96 pptV of CH₃I (b).

(a) WDL-I₂

(b) WDL-CH₃I

(c) WDM-I₂

(d) WDM-CH₃I

(e) WDH-I₂

(f) WDH-CH₃I

Fig. 3. Iodine nitroxides normalized mass speciation evolution, 2013 January 1st, for iodine release at 7 am with 0.98 pptV (a), 98 pptV (c), 9800 pptV (e) of I₂ and 1.96 pptV (b), 196 pptV (d), 19600 pptV (f) of CH₃I.

(a) WDM-I₂

(b) WNM-I₂

Fig. 4. Iodine reaction scheme for 98 pptV of I₂ release, 2013 January 1st, at 7 am (a) and 6 pm (b).

(a) WDM-I₂

(b) WNM-I₂

(c) SDM-I₂

(d) SNM-I₂

Fig. 5. Family mass evolution of iodine, for an iodine release of 98 pptV, 2013 January 1st, at 7 am (a) and 6 pm (b), 2013 August 8th at 4 am (c) and 9 pm (d).

(a) SDM-I₂

(b) SDM-CH₃I

Fig. 6. Family mass evolution of iodine, 2013 August 8th, for an iodine release at 4 am with 98 pptV of I₂ (a) and 196 pptV of CH₃I (b).

(a) SDM-I₂

(b) SDM-CH₃I

Fig. 7. Iodine reaction scheme, 2013 August 8th, for an iodine release at 4 am with 98 pptV of I₂ (a) and 196 pptV of CH₃I (b).

Fig. 8. Iodine oxide normalized mass speciation evolution, 2013 August 8th, for an iodine release at 4 am with 98 pptV of I₂ (a) and 196 pptV of CH₃I (b).

(a) WDL-CH₃I

(b) WDM-CH₃I

(c) WDH-CH₃I

Fig. 9. Organic iodine normalized mass speciation evolution, 2013 January 1st, for iodine release at 7 am with 1.96 pptV (a), 196 pptV (b) and 19600 pptV (c) of CH₃I.

(a) SDM-I₂

(b) SNM-I₂

Fig. 10. Iodine reaction scheme for 98 pptV of I₂ release, 2013 August 8th, at 4 am (a) and 9 pm (b).

This work (SDM-I₂)

Saiz-Lopez et al. 2016 (SDM-I₂)

Fig. 11. Family mass evolution of iodine, for an iodine release of 98 pptV, 2013 August 8th at 4 am.

This work (WDM-I₂)

Saiz-Lopez et al. 2016 (WDM-I₂)

Fig. 12. Family mass evolution of iodine, for an iodine release of 98 pptV, 2013 January 1st, at 7 am.

Appendix A.1: Organic iodine gas-phase mechanism

#	Reaction	Rate coefficient (s ⁻¹) or (cm ³ molecule ⁻¹ s ⁻¹) or (cm ⁶ molecule ⁻² s ⁻¹)	Reference	IRACM reaction
1	HI + CH ₂ =CH ₂ → CH ₃ CH ₂ I	$5.50 \times 10^{-16} \exp(-14560/T)$	(Benson and Bose, 1962)	HI + ETE → I_ETH
2	HI + CH ₃ CH=CHCH ₃ → CH ₃ CHICH ₂ CH ₃	$3.02 \times 10^{-15} \exp(-10605/T)$	(Nangia and Benson, 1964)	HI + OLI → I_HC3
3	HI + cyclopentene → iodocyclopentane	$4.17 \times 10^{-13} \exp(-13477/T)$	(Furuyama et al., 1970a)	HI + OLI → I_HC5
4	HI + CH ₂ =CHCH ₃ → CH ₂ ICH ₂ CH ₃	$1.29 \times 10^{-13} \exp(-11805/T)$	(Bose and Benson, 1962)	HI + OLT → I_HC3
5	HI + i-C ₄ H ₈ → t-C ₄ H ₉ I	$5.25 \times 10^{-15} \exp(-9061/T)$	(Bose and Benson, 1963)	HI + OLT → I_HC3
6	I + benzaldehyde → HI + benzoyl	$1.99 \times 10^{-11} \exp(-8399/T)$	(Solly and Benson, 1971)	I + ALD → HI + ALDR
7	I + CH ₂ CHCH(O) → HI + CH ₂ CHCO	$2.09 \times 10^{-11} \exp(-8459/T)$	(Alfassi and Golden, 1973b)	I + ALD → HI + ALDR
8	I + CH ₄ → HI + CH ₃	$3.82 \times 10^{-11} \exp(-16365/T)$	(Mečiarová et al., 2011)	I + CH ₄ → HI + MR
9	I + benzene → HI + phenyl	$1.10 \times 10^{-8} \exp(-21540/T)$	(Rodgers et al., 1967)	I + CSL → HI + CSLR
10	I + phenyl → HI + cyclopentadienyl	$4.78 \times 10^{-13} \exp(-5373/T)$	(Furuyama et al., 1971)	I + DIEN → HI + DIENR
11	I + CH ₃ CH ₃ → HI + CH ₃ CH ₂	$2.21 \times 10^{-10} \exp(-13237/T)$	(Knox and Musgrave, 1967)	I + ETH → HI + ETHR
12	I + CH ₃ C≡CH → HI + CH ₃ C≡C	$3.24 \times 10^{-10} \exp(-12154/T)$	(Walsh, 1971)	I + HC3 → HI + HC3R
13	I + CH ₃ OCH ₃ → HI + CH ₃ OCH ₂	$5.25 \times 10^{-10} \exp(-11706/T)$	(Cruickshank and Benson, 1969b)	I + HC3 → HI + HC3R
14	I + CH ₃ OH → HI + CH ₂ OH	$5.25 \times 10^{-10} \exp(-13116/T)$	(Cruickshank and Benson, 1969a)	I + HC3 → HI + HC3R
15	I + cyclobutane → HI + cyclobutyl	$7.59 \times 10^{-10} \exp(-13477/T)$	(McMillen et al., 1972)	I + HC3 → HI + HC3R
16	I + i-C ₄ H ₁₀ → HI + t-C ₄ H ₉	$3.32 \times 10^{-10} \exp(-11305/T)$	(Knox and Musgrave, 1967)	I + HC3 → HI + HC3R
17	I + CH ₃ CH ₂ CH ₃ → HI + i-C ₃ H ₇	$1.83 \times 10^{-10} \exp(-12006/T)$	(Knox and Musgrave, 1967)	I + HC3 → HI + HC3R
18	I + CH ₃ CH ₂ CH ₃ → HI + n-C ₃ H ₇	$1.26 \times 10^{-9} \exp(-14921/T)$	(Knox and Musgrave, 1967)	I + HC3 → HI + HC3R
19	I + cyclopropane → CH ₂ CH ₂ CH ₂ I	$1.22 \times 10^{-11} \exp(-8705/T)$	(Ogg and Priest, 1939)	I + HC3 → I_HC3R
20	I + cyclopentane → HI + cyclopentyl	$1.48 \times 10^{-9} \exp(-12515/T)$	(Furuyama et al., 1970b)	I + HC5 → HI + HC5R
21	I + i-C ₃ H ₇ OH → HI + CH ₃ CHOCH ₃	$1.94 \times 10^{-13} \exp(-10305/T)$	(Walsh and Benson, 1966b)	I + HC5 → HI + HC3R

#	Reaction	Rate coefficient (s ⁻¹) or (cm ³ molecule ⁻¹ s ⁻¹) or (cm ⁶ molecule ⁻² s ⁻¹)	Reference	IRACM reaction
22	I + tetrahydrofuran → HI + tetrahydrofuranyl	$7.77 \times 10^{-10} \exp(-10814/T)$	(Cruickshank and Benson, 1969c)	I + HC8 → HI + HC8R
23	I + HC(O)H → HI + HC(O)	$1.38 \times 10^{-10} \exp(-8774/T)$	(Walsh and Benson, 1966a)	I + HCHO → HI + HCHOR
24	I + CH ₃ CH ₂ C(O)CH ₃ → HI + CH ₃ CHC(O)CH ₃	$9.47 \times 10^{-11} \exp(-11066/T)$	(Solly et al., 1970a)	I + KET → HI + KETR
25	I + CH ₃ C(O)CH ₃ → HI + CH ₂ C(O)CH ₃	$2.62 \times 10^{-10} \exp(-13959/T)$	(Solly et al., 1970b)	I + KET → HI + KETR
26	I + CH ₃ O ₂ → CH ₃ OOI	2.00×10^{-11}	(Dillon et al., 2006)	I + MO2 → I_OP1
27	I + cyclopentene → HI + cyclopentyl	$2.96 \times 10^{-11} \exp(-6161/T)$	(Furuyama et al., 1970a)	I + OLI → HI + OLIR
28	I + CH ₂ =CHCH ₂ OH → HI + CH ₂ =CHCHOH	$5.25 \times 10^{-12} \exp(-5691/T)$	(Alfassi and Golden, 1973a)	I + OLT → HI + OLTR
29	I + CH ₂ =CHCH ₃ → HI + CH ₂ =CHCH ₂	$2.96 \times 10^{-11} \exp(-9085/T)$	(Golden et al., 1966)	I + OLT → HI + OLTR
30	I + toluene → HI + benzyl	$4.47 \times 10^{-13} \exp(-72539/T)$	(Walsh et al., 1966)	I + TOL → HI + TOLR
31	IO + C ₂ H ₄ → products	2.00×10^{-16}	(Maguin et al., 1991)	IO + ETE → PROD
32	IO + C ₂ H ₅ O ₂ → products	1.40×10^{-10}	(Enami et al., 2006)	IO + ETHP → PROD
33	IO + CH ₃ O ₂ → products	$1.30 \times 10^{-10} \exp(-168/T)$	(Enami et al., 2006)	IO + MO2 → PROD
34	IO + CH ₂ =CHCH ₃ → products	2.00×10^{-16}	(Maguin et al., 1991)	IO + OLT → PROD
35	IO + HCOOH → HOI + HCOO	2.91×10^{-15}	(Buben et al., 1995)	IO + ORA1 → HOI + ORA1R
36	I ₂ + cyclopentane → 2 HI + cyclopentyl	$1.48 \times 10^{-9} \exp(-12515/T)$	(Furuyama et al., 1970b)	I2 + HC5 → 2 HI + HC5R
37	CH ₃ C(O)I → I + CH ₃ C(O)	$1.00 \times 10^{13} \exp(-25511/T)$	(Butler and Polanyi, 1943)	I_ALD → I + ALDR
38	CH ₃ I + H → HI + CH ₃	$6.30 \times 10^{-11} \exp(-602/T)$	(Yuan et al., 1997)	I_CH4 + H → HI + MR
39	CH ₃ I + OH → CH ₂ I + H ₂ O	$4.10 \times 10^{-12} \exp(-1239/T)$	(Zhang et al., 2011b)	I_CH4 + H → I_MR + H2O
40	CH ₃ I + NO ₃ → CH ₂ I + HNO ₃	$9.10 \times 10^{-11} \exp(-1564/T)$	(Nakano et al., 2008)	I_CH4 + NO3 → I_MR + HNO3

#	Reaction	Rate coefficient (s ⁻¹) or (cm ³ molecule ⁻¹ s ⁻¹) or (cm ⁶ molecule ⁻² s ⁻¹)	Reference	IRACM reaction
	CH ₃ I + O(³ P) → IO + CH ₃	1.00 × 10 ⁻¹¹ exp(160/T) × 0.59		I_CH4 + O3P → IO + MR
	→ CH ₂ I + OH	1.00 × 10 ⁻¹¹ exp(160/T) × 0.21		→ I_MR + HO
41	→ H + I + HC(O)H	1.00 × 10 ⁻¹¹ exp(160/T) × 0.09	(Gilles et al., 1996)	→ H + I + HCHO
	→ I + CH ₃ O	1.00 × 10 ⁻¹¹ exp(160/T) × 0.04		→ I + HC3R
	→ HI + HC(O)H	1.00 × 10 ⁻¹¹ exp(160/T) × 0.07		→ HI + HCHO
42	CH ₃ I → I + CH ₃	5.62 × 10 ¹³ exp(-27797/T)	(Skorobogatov et al., 1994)	I_CH4 → I + MR
43	iodobenzene + H → HI + phenyl	1.45 × 10 ⁻¹⁸ T ^{2.5} exp(73/T)	(Gao et al., 2008)	I_CSL + H → HI + CSLR
44	iodobenzene + OH → products	1.32 × 10 ⁻¹²	(Wallington et al., 1987)	I_CSL + HO → PROD
45	iodobenzene → products	1.98 × 10 ¹¹ exp(-23104/T)	(Kumaran et al., 1997)	I_CSL → PROD
46	CH ₂ =CHI → I + CH ₂ =CH	4.00 × 10 ¹⁵ exp(-33574/T)	(Shilov and Sabirova, 1964)	I_ETE → I + ETER
47	CH ₃ CH ₂ I + H → CH ₃ CH ₂ + HI	1.10 × 10 ⁻¹⁰ exp(-708/T)	(Yuan et al., 1997)	I_ETH + H → ETHR + HI
48	CH ₃ CH ₂ I + OH → CH ₂ CH ₂ I + H ₂ O	5.55 × 10 ⁻¹² exp(-830/T)	(Zhang et al., 2012)	I_ETH + HO → I_ETHR + H2O
49	CH ₃ CH ₂ I + O(³ P) → products	1.58 × 10 ⁻¹¹ exp(239/T)	(Teruel et al., 2004)	I_ETH + O3P → PROD
50	CH ₃ CH ₂ I → CH ₃ CH ₂ + I	6.34 × 10 ⁹ exp(-15884/T)	(Kumaran et al., 1996)	I_ETH → ETHR + I
51	n-C ₃ H ₇ I + H → n-C ₃ H ₇ + HI	1.00 × 10 ⁻¹³	(Rebbert et al., 1973)	I_HC3 + H → HC3R + HI
52	i-C ₃ H ₇ I + H → i-C ₃ H ₇ + HI	1.40 × 10 ⁻¹¹	(Yuan et al., 1997)	I_HC3 + H → HC3R + HI
53	t-C ₃ H ₇ I + H → t-C ₃ H ₇ + HI	2.00 × 10 ⁻¹¹	(Yuan et al., 1997)	I_HC3 + H → HC3R + HI
	CH ₂ ICH ₂ CH ₃ + OH → CH ₂ CH ₂ CH ₂ I + H ₂ O	1.65 × 10 ⁻¹¹ exp(-781/T) × 0.09 ^a		I_HC3 + HO → I_HC3R + H2O
54	→ CH ₃ CH ₂ CHI + H ₂ O	1.65 × 10 ⁻¹¹ exp(-781/T) × 0.37 ^a	(Zhang et al., 2012)	→ I_HC3R + H2O
	→ CH ₃ CHCH ₂ I + H ₂ O	1.65 × 10 ⁻¹¹ exp(-781/T) × 0.54 ^a		→ I_HC3R + H2O
55	CH ₃ CHICH ₃ + OH → CH ₂ CHICH ₃ + H ₂ O	7.58 × 10 ⁻¹² exp(-531/T) × 0.22 ^a		I_HC3 + HO → I_HC3R + H2O
	→ CH ₃ CICH ₃ + H ₂ O	7.58 × 10 ⁻¹² exp(-531/T) × 0.78 ^c	(Zhang et al., 2012)	→ I_HC3R + H2O

#	Reaction	Rate coefficient (s ⁻¹) or (cm ³ molecule ⁻¹ s ⁻¹) or (cm ⁶ molecule ⁻² s ⁻¹)	Reference	IRACM reaction
56	CH ₂ ICH ₂ CH ₃ + O(³ P) → HOI + CH ₂ =CHCH ₃ → IO + CH ₂ CH ₂ CH ₃	1.10 × 10 ⁻¹¹ exp(367/T) × 0.79 1.10 × 10 ⁻¹¹ exp(367/T) × 0.21	(Teruel et al., 2004)	I_HC3 + O3P → HIO + OLT → IO + HC3R
57	CH ₃ CHICH ₃ + O(³ P) → HOI + CH ₂ =CHCH ₃ → IO + CH ₃ CHCH ₃	1.84 × 10 ⁻¹¹ exp(296/T) × 0.79 1.84 × 10 ⁻¹¹ exp(296/T) × 0.21	(Teruel et al., 2004)	I_HC3 + O3P → HIO + OLT → IO + HC3R
58	s-C ₄ H ₉ I → HI + CH ₃ CH=CHCH ₃	1.58 × 10 ¹⁵ exp(-24067/T)	(Holmes and Maccoll, 1963)	I_HC3 → HI + OLT
59	i-C ₃ H ₇ I → HI + CH ₂ =CHCH ₃	4.68 × 10 ¹³ exp(-22623/T)	(Tsang, 1964)	I_HC3 → HI + OLT
60	t-C ₄ H ₉ I → HI + i-C ₄ H ₈	7.94 × 10 ¹³ exp(-19735/T)	(Hippler et al., 1991)	I_HC3 → HI + OLT
61	CH ₂ CH ₂ CH ₂ I → I + cyclopropane	3.31 × 10 ⁻¹¹ exp(-8104/T)	(Benson, 1961)	I_HC3R → I + I_HC3
62	iodocyclopentane → HI + cyclopentene	2.00 × 10 ¹³	(Furuyama et al., 1970b)	I_HC5 → HI + OLI
63	CH ₂ I + NO ₂ → products	8.51 × 10 ⁻⁸ T ^{-1.45}	(Eskola et al., 2006)	I_MR + NO2 → PROD
64	CH ₂ I + O ₂ → CH ₂ IO ₂	1.82 × 10 ⁻¹²	(Sheps, 2013)	I_MR + O2 → I_MO2
65	CH ₂ I + O ₂ → HC(O)H + IO	4.00 × 10 ⁻¹³	(Enami et al., 2004)	I_MR + O2 → HCHO + IO
66	CH ₂ =CHCH ₂ I + OH → products	6.00 × 10 ⁻¹¹	(Albaladejo et al., 2003)	I_OLT + HO → PROD
67	CH ₂ =CHCH ₂ I + NO ₃ → products	3.91 × 10 ⁻¹⁴	(Martinez et al., 1996)	I_OLT + NO3 → PROD
68	CH ₂ =CHCH ₂ I + O ₃ → products	8.17 × 10 ⁻¹⁴ exp(-2992/T)	(Gai et al., 2009)	I_OLT + O3 → PROD
69	CH ₂ =CHCH ₂ I → I + CH ₂ =CHCH ₂	1.00 × 10 ¹³ exp(-19614/T)	(Butler and Polanyi, 1943)	I_OLT → I + OLTR
70	iodomethylbenzene → I + benzyl	6.03 × 10 ¹⁴	(Mueller-Markgraf and Troe, 1988)	I_TOL → I + TOLR
71	CH ₂ I ₂ + NO ₃ → products	4.00 × 10 ⁻¹³	(Nakano et al., 2006)	I2_CH4 + NO3 → PROD
72	CH ₂ I ₂ + O(³ P) → products	7.36 × 10 ⁻¹¹	(Teruel et al., 2004)	I2_CH4 + O3P → PROD
73	CH ₂ I ₂ → I + CH ₂ I	2.51 × 10 ¹⁵ exp(-21299/T)	(Saito et al., 1980)	I2_CH4 → I + I_MR
74	CHI=CHI → I ₂ + C ₂ H ₂	3.11 × 10 ¹² exp(-23104/T)	(Furuyama et al., 1969c)	I2_ETE → I2 + HC3
75	CHI ₃ → I + CHI ₂	1.00 × 10 ¹³ exp(-18652/T)	(Butler et al., 1945)	I3_CH4 → I + I2_MR

#	Reaction	Rate coefficient (s ⁻¹) or (cm ³ molecule ⁻¹ s ⁻¹) or (cm ⁶ molecule ⁻² s ⁻¹)	Reference	IRACM reaction
76	CH ₃ CH ₂ I + NO ₃ → products	$9.48 \times 10^{-27} \exp(-654/T)$	(Bai et al., 2015)	I_ETH + NO3 → PROD
77	CH ₂ I ₂ + OH → products	$4.20 \times 10^{-11} \exp(-670/T)$	(Zhang et al., 2011a)	I2_CH4 + HO → PROD
78	CH ₃ CHI + O ₂ → CH ₃ CHO ₂ + I	8.00×10^{-12}	(Sheps et al., 2014)	I_ETHR + O2 → ETHP + I
79	HI + CH ₂ I → I + CH ₃ I	$1.69 \times 10^{-12} \exp(192/T)$	(Seetula and Gutman, 1991)	HI + I_MR → I + I_CH4
80	I + CH ₃ C(O)I → I ₂ + CH ₃ C(O)	$1.32 \times 10^{-10} \exp(-7353/T)$	(O'Neal and Benson, 1962b)	I + I_ALD → I2 + ALDR
81	I + CH ₃ I → I ₂ + CH ₃	$4.17 \times 10^{-10} \exp(-1030/T)$	(Flowers and Benson, 1963)	I + I_CH4 → I2 + MR
82	I + iodobenzene → I ₂ + phenyl	$3.80 \times 10^{-10} \exp(-14320/T)$	(Rodgers et al., 1967)	I + I_CSL → I2 + CSLR
83	I + iodocyclopentadiene → I ₂ + cyclopentadienyl	$2.09 \times 10^{-12} \exp(-204/T)$	(Furuyama et al., 1971)	I + I_DIEN → I2 + DIENR
84	I + CH ₃ CH ₂ I → I ₂ + CH ₃ CH ₂	$1.69 \times 10^{-10} \exp(-8604/T)$	(Hartley and Benson, 1963)	I + I_ETH → I2 + ETHR
85	I + s-C ₄ H ₉ I → HI + I + CH ₃ CH=CHCH ₃	$4.90 \times 10^{-12} \exp(-9014/T)$	(Nangia and Benson, 1964)	I + I_HC3 → HI + I + OLI
86	I + iodomethylcyclopropane → I ₂ + methylcyclopropyl	$4.17 \times 10^{-10} \exp(-8454/T)$	(McMillen et al., 1971)	I + I_HC3 → I2 + HC3R
87	I + n-C ₃ H ₇ I → I ₂ + n-C ₃ H ₇	$3.25 \times 10^{-10} \exp(-9315/T)$	(Benson and O'Neal, 1961)	I + I_HC3 → I2 + HC3R
88	I + t-C ₄ H ₉ I → I ₂ + t-C ₄ H ₉ I	$8.32 \times 10^{-11} \exp(-6543/T)$	(Teranishi and Benson, 1963)	I + I_HC3 → I2 + HC3R
89	I + iodocyclopentane → I ₂ + cyclopentyl	$8.32 \times 10^{-10} \exp(-8564/T)$	(Furuyama et al., 1970b)	I + I_HC5 → I2 + HC5R
90	I + CH ₂ I → CH ₂ I ₂	1.33×10^{-10}	(Hunter and Kristjansson, 1982)	I + I_MR → I2_CH4
91	I + CH ₃ OOI → I ₂ + CH ₃ O ₂	1.50×10^{-10}	(Dillon et al., 2006)	I + I_OP1 → I2 + MO2
92	I + iodomethylbenzene → I ₂ + benzyl	$9.33 \times 10^{-13} \exp(-1760/T)$	(Walsh et al., 1966)	I + I_TOL → I2 + TOLR
93	I + CH ₂ I ₂ → I ₂ + CH ₂ I	$4.68 \times 10^{-10} \exp(-7604/T)$	(Furuyama et al., 1969a)	I + I2_CH4 → I2 + I_MR
94	I + CHI=CHI → products	$1.18 \times 10^{-12} \exp(-5542/T)$	(Golden and Benson, 1969)	I + I2_ETE → PROD
95	I + ICH ₂ CH ₂ CH ₂ I → I ₂ + CH ₂ CH ₂ CH ₂ I	$1.66 \times 10^{-10} \exp(-9814/T)$	(Benson, 1961)	I + I2_HC3 → I2 + I_HC3R
96	I + CHI ₃ → I ₂ + CHI ₂	$9.33 \times 10^{-10} \exp(-4853/T)$	(Furuyama et al., 1969b)	I + I3_CH4 → I2 + I2_MR
97	I ₂ + CH ₂ CH ₂ CH ₂ I → I + ICH ₂ CH ₂ CH ₂ I	$5.25 \times 10^{-12} \exp(-251/T)$	(Benson, 1961)	I2 + I_HC3R → I + I2_HC3

#	Reaction	Rate coefficient (s ⁻¹) or (cm ³ molecule ⁻¹ s ⁻¹) or (cm ⁶ molecule ⁻² s ⁻¹)	Reference	IRACM reaction
98	I ₂ + CH ₂ I → I + CH ₂ I ₂	3.32 × 10 ⁻¹⁰	(Hunter and Kristjansson, 1982)	I ₂ + I_MR → I + I ₂ _CH4
99	IO + CH ₃ I → HOI + CH ₂ I	6.69 × 10 ⁻²⁰ T ^{2.09} exp(-26835/T)	(Cours et al., 2013)	IO + I_CH4 → HIO + I_MR
100	CH ₂ IO ₂ + CH ₂ IO ₂ → 0.5 CH ₂ IOH + 0.5 HC(O)I + CH ₂ IO + O ₂	9.00 × 10 ⁻¹¹	(Sehested et al., 1994)	I_MO2 + I_MO2 → 0.5 I_HC3 + 0.5 I_HCHO + I_HC3R + O2
101	HI + CH ₃ C(O) → I + CH ₃ CH(O)	2.25 × 10 ⁻¹² exp(-754/T)	(O'Neal and Benson, 1962a)	HI + ALDR → I + ALD
102	HI + phenyl → I + benzene	2.89 × 10 ⁻¹² exp(-200/T)	(Rodgers et al., 1967)	HI + CSLR → I + CSL
103	HI + cyclopentadienyl → I + cyclopentadiene	5.25 × 10 ⁻¹⁴ exp(-503/T)	(Furuyama et al., 1971)	HI + DIENR → I + DIEN
104	HI + C ₂ H ₃ → I + C ₂ H ₄	7.26 × 10 ⁻¹² exp(383/T)	(Seetula, 1991)	HI + ETER → I + ETE
105	HI + CH ₃ CH ₂ → I + CH ₃ CH ₃	1.12 × 10 ⁻²⁰ T ^{2.92} exp(-429/T)	(Leplat et al., 2015)	HI + ETHR → I + ETH
106	HI + CH ₂ OH → I + CH ₃ OH	2.71 × 10 ⁻¹² exp(-577/T)	(Seetula and Gutman, 1992)	HI + HC3R → I + HC3
107	HI + i-C ₃ H ₇ → I + CH ₃ CH ₂ CH ₃	1.94 × 10 ⁻¹¹ exp(-744/T)	(Leplat and Rossi, 2014a)	HI + HC3R → I + HC3
108	HI + n-C ₃ H ₇ → I + CH ₃ CH ₂ CH ₃	6.49 × 10 ⁻¹¹ exp(-1333/T)	(Leplat and Rossi, 2014a)	HI + HC3R → I + HC3
109	HI + s-C ₄ H ₉ → I + n-C ₄ H ₁₀	3.20 × 10 ⁻¹² exp(708/T)	(Seetula et al., 1990)	HI + HC3R → I + HC3
110	HI + t-C ₄ H ₉ → I + i-C ₄ H ₁₀	2.00 × 10 ⁻¹¹ exp(-1020/T)	(Leplat and Rossi, 2014b)	HI + HC3R → I + HC3
111	HI + cyclopentyl → I + cyclopentane	6.61 × 10 ⁻¹² exp(-503/T)	(Furuyama et al., 1970b)	HI + HC5R → I + HC5
112	HI + HC(O) → I + HC(O)H	3.09 × 10 ⁻¹² exp(-98/T)	(Becerra et al., 1997)	HI + HCHOR → I + HCHO
113	HI + CH ₃ → I + CH ₄	4.50 × 10 ⁻¹² exp(144/T)	(Seetula et al., 1990)	HI + MR → I + CH4
114	HI + cyclopentenyl → I + cyclopentene	1.66 × 10 ⁻¹² exp(-503/T)	(Furuyama et al., 1970a)	HI + OLIR → I + OLI
115	HI + CH ₂ =CHCH ₂ → I + CH ₂ =CHCH ₃	1.69 × 10 ⁻¹¹ exp(-2466/T)	(Rossi and Golden, 1979)	HI + OLTR → I + OLT
116	HI + benzyl → I + toluene	2.96 × 10 ⁻¹⁴ exp(-754/T)	(Walsh et al., 1966)	HI + TOLR → I + TOL
117	I + phenyl → iodobenzene	2.49 × 10 ⁻¹¹	(Robaugh and Tsang, 1986)	I + CSLR → I_CSL
118	I + C ₂ H ₃ → CH ₂ =CHI	7.31 × 10 ⁻¹² exp(-503/T)	(Lifshitz et al., 2008)	I + ETER → I_ETE

#	Reaction	Rate coefficient (s ⁻¹) or (cm ³ molecule ⁻¹ s ⁻¹) or (cm ⁶ molecule ⁻² s ⁻¹)	Reference	IRACM reaction
119	I + CH ₃ CH ₂ → C ₂ H ₅ I	1.16 × 10 ⁻¹¹	(Hunter and Kristjansson, 1982)	I + ETHR → I_ETH
120	I + CH ₃ O → HI + HC(O)H	8.50 × 10 ⁻¹¹	(Shah et al., 2001)	I + HC3R → HI + HCHO
121	I + CH ₃ → CH ₃ I	9.96 × 10 ⁻¹²	(Hunter and Kristjansson, 1982)	I + MR → I_CH4
122	I + CH ₂ =CHCH ₂ → CH ₂ =CHCH ₂ I	1.60 × 10 ⁻¹⁰	(Jenkin et al., 1993)	I + OLTR → I_OLT
123	I + benzyl → iodomethylbenzene	8.32 × 10 ⁻¹¹	(Mueller-Markgraf and Troe, 1988)	I + TOLR → I_TOL
124	I ₂ + CH ₃ C(O) → I + CH ₃ C(O)I	6.61 × 10 ⁻¹²	(O'Neal and Benson, 1962a)	I ₂ + ALDR → I + I_ALD
125	I ₂ + phenyl → I + iodobenzene	9.13 × 10 ⁻¹²	(Rodgers et al., 1967)	I ₂ + CSLR → I + I_CSL
126	I ₂ + cyclopentadienyl → I + iodocyclopentadiene	2.09 × 10 ⁻¹³	(Furuyama et al., 1971)	I ₂ + DIENR → I + I_DIEN
127	I ₂ + CH ₃ CH ₂ → I + CH ₃ CH ₂ I	5.00 × 10 ⁻¹¹	(Hayes and Strong, 1986)	I ₂ + ETHR → I + I_ETH
128	I ₂ + i-C ₃ H ₇ → I + i-C ₃ H ₇ I	3.30 × 10 ⁻¹¹	(Christie and Frost, 1965)	I ₂ + HC3R → I + I_HC3
129	I ₂ + n-C ₃ H ₇ I → I + n-C ₃ H ₇ I	5.00 × 10 ⁻¹¹	(Hayes and Strong, 1986)	I ₂ + HC3R → I + I_HC3
130	I ₂ + cyclopentyl → I + iodocyclopentane	2.09 × 10 ⁻¹¹	(Furuyama et al., 1970b)	I ₂ + HC5R → I + I_HC5
131	I ₂ + CH ₃ → I + CH ₃ I	5.81 × 10 ⁻¹²	(Hunter and Kristjansson, 1982)	I ₂ + MR → I + I_CH43
132	I ₂ + cyclopentenyl → I + iodocyclopentene	5.25 × 10 ⁻¹²	(Furuyama et al., 1970a)	I ₂ + OLIR → I + I_OLI
133	I ₂ + CH ₂ =CHCH ₂ → CH ₂ =CHCH ₂ I + I	1.20 × 10 ⁻¹¹	(Jenkin et al., 1993)	I ₂ + OLTR → I + I_OLT
134	I ₂ + benzyl → I + iodomethylbenzene	9.33 × 10 ⁻¹⁴	(Walsh et al., 1966)	I ₂ + TOLR → I + I_TOL
135	IO + CH ₃ O → HOI + HC(O)H	4.00 × 10 ⁻¹¹	(Shah et al., 2001)	IO + HC3R → HIO + HCHO
136	CH ₃ I + CH ₃ → CH ₂ I + CH ₄	1.05 × 10 ⁻¹² exp(-6/T)	(Saito et al., 1980)	I_CH4 + MR → I_MR + CH4
137	iodobenzene + phenyl → products	2.00 × 10 ⁻¹¹	(Alecú et al., 2007)	I_CSL + CSLR → PROD
138	CH ₃ CH ₂ I + CH ₃ → CH ₃ I + CH ₃ CH ₂	1.32 × 10 ⁻¹² exp(-3/T)	(Sidebottom and Treacy, 1984)	I_ETH + MR → I_CH4 + ETHR
139	CH ₂ I + CH ₃ → CH ₃ CH ₂ I	5.23 × 10 ⁻¹¹	(Saito et al., 1980)	I_MR + MR → I_ETH

^a Branching ratio from (Cotter et al., 2003).

Appendix A.2: Inorganic iodine gas-phase mechanism

#	Reaction	Rate coefficient ^a (s ⁻¹) or (cm ³ molecule ⁻¹ s ⁻¹) or (cm ⁶ molecule ⁻² s ⁻¹)	Reference
1	HI + H → I + H ₂	$6.08 \times 10^{-11} \exp(-361/T)$	(Umemoto et al., 1988)
2	HI + HI → I ₂ + H ₂	$4.25 \times 10^{-11} \exp(-22021/T)$	(Baulch et al., 1981)
3	HI + OH → HOI + H	$1.49 \times 10^{-18} T^{2.28} \exp(-12394/T)$	(Xerri et al., 2012)
4	HI + OH → I + H ₂ O	$1.60 \times 10^{-11} \exp(440/T)$	(Atkinson et al., 2007)
5	HI + I → I ₂ + H	$9.70 \times 10^{-16} T^{1.72} \exp(-17930/T)$	(Canneaux et al., 2010)
6	HI + IO → HOI + I	$3.01 \times 10^{-19} T^{2.36} \exp(-673/T)$	(Hammaecher et al., 2011)
7	HI + NO ₂ → I + HONO	$3.60 \times 10^{-14} \exp(-3249/T)$	(Diao and Chu, 2001)
8	HI + NO ₃ → I + HNO ₃	$1.30 \times 10^{-12} \exp(-1829/T)$	(Lancar et al., 1991)
9	HI + O(³ P) → OH + I	$6.68 \times 10^{-11} \exp(-999/T)$	(Singleton and Cvetanović, 1978)
10	HI + O ₂ → I + HO ₂	$3.30 \times 10^{-12} \exp(-11131/T)$	(Shum and Benson, 1983)
11	HOI + H → HI + OH	$1.89 \times 10^{-15} T^{1.49} \exp(1155/T)$	(Xerri et al., 2012)
12	HOI + H → I + H ₂ O	$9.96 \times 10^{-16} T^{1.55} \exp(-1576/T)$	(Xerri et al., 2012)
13	HOI + H → IO + H ₂	$1.40 \times 10^{-23} T^{3.66} \exp(-2166/T)$	(Hammaecher et al., 2011)
14	HOI + HNO ₂ → INO ₂ + H ₂ O	8.30×10^{-16}	(Vickis, 1989)
15	HOI + OH → IO + H ₂ O	$3.60 \times 10^{-27} T^{4.41} \exp(2395/T)$	(Hammaecher et al., 2011)
16	HOI + I → HI + IO	$3.80 \times 10^{-18} T^{2.29} \exp(-13237/T)$	(Hammaecher et al., 2011)
17	HOI + I → I ₂ + OH	$2.61 \times 10^{-16} T^{1.72} \exp(-5283/T)$	(Xerri et al., 2012)
18	HOI + O(³ P) → IO + OH	$2.81 \times 10^{-27} T^{4.65} \exp(-300/T)$	(Hammaecher et al., 2011)
19	HOI + O ₂ → IO + HO ₂	0.06	(Jenkin et al., 1991)
20	I + H (+M) → HI (+ M)	$1.3 \times 10^{-31} (T/298)^{1.87}$	(Lifshitz et al., 2008)
21	I + H ₂ → HI + H	$4.52 \times 10^{-10} \exp(-17087/T)$	(Michael et al., 2000)

#	Reaction	Rate coefficient ^a (s ⁻¹) or (cm ³ molecule ⁻¹ s ⁻¹) or (cm ⁶ molecule ⁻² s ⁻¹)	Reference
22	I + H ₂ O → HI + OH	$5.20 \times 10^{-17} T^{2.26} \exp(-21780/T)$	(Canneaux et al., 2010)
23	I + H ₂ O → HOI + H	$4.20 \times 10^{-18} T^{2.48} \exp(-36462/T)$	(Xerri et al., 2012)
24	I + H ₂ O ₂ → HOI + OH	$3.11 \times 10^{-20} T^{2.95} \exp(-7244/T)$	(Fortin et al., 2018)
25	I + OH → HI + O(³ P)	$4.70 \times 10^{-20} T^{1.70} \exp(-14922/T)$	(Canneaux et al., 2010)
26	I + OH → IO + H	$2.51 \times 10^{-10} \exp(-32250/T)$	(Garrett and Truhlar, 1979)
27	I + HO ₂ → HI + O ₂	$1.47 \times 10^{-11} \exp(-1155/T)$	(Jenkin et al., 1990)
28	I + I (+ M) → I ₂ (+ M)	$k_0 = 1.20 \times 10^{-32}$, $k_\infty = 2.99 \times 10^{-11}$, $F_c = 1$	(Hippler et al., 1973)
29	I + I ₂ O → I ₂ + IO	3.82×10^{-11}	(Hippler et al., 1973)
30	I + INO → I ₂ + NO	1.66×10^{-10}	(Basco and Hunt, 1978)
31	I + INO ₂ → I ₂ + NO ₂	8.32×10^{-11}	(van den Bergh and Troe, 1976)
32	I + IO → I ₂ O	1.69×10^{-10}	(Bloss et al., 2001)
33	I + IONO ₂ → I ₂ + NO ₃	$9.10 \times 10^{-11} \exp(-145/T)$	(Kaltsoyannis and Plane, 2008)
34	I + NO (+M) → INO (+ M)	$k_0 = 1.80 \times 10^{-32} (T/300)^{-1}$, $k_\infty = 1.70 \times 10^{-11}$, $F_c = 0.6$	(van den Bergh and Troe, 1976)
35	I + NO ₂ (+M) → INO ₂ (+M)	$k_0 = 3.20 \times 10^{-31}$, $k_\infty = 1.10 \times 10^{-10}$, $F_c = 0.48$	(Tucceri et al., 2005)
36	I + NO ₃ → IO + NO ₂	1.00×10^{-10}	(Dillon et al., 2008)
37	I + O ₃ → IO + O ₂	$2.10 \times 10^{-11} \exp(-830/T)$	(Atkinson et al., 2007)
38	I ₂ + H → HI + I	$6.59 \times 10^{-10} \exp(-20/T)$	(Lorenz et al., 1979)
39	I ₂ + H ₂ → HI + HI	$1.73 \times 10^{-10} \exp(-20457/T)$	(Sullivan, 1959)
40	I ₂ + OH → HOI + I	$1.97 \times 10^{-10} \exp(-20/T)$	(IUPAC, 2007)
41	I ₂ + NO ₃ → I + IONO ₂	1.50×10^{-12}	(Chambers et al., 1992)
42	I ₂ + O → I + IO	1.20×10^{-10}	(Tucceri et al., 2005)

#	Reaction	Rate coefficient ^a (s ⁻¹) or (cm ³ molecule ⁻¹ s ⁻¹) or (cm ⁶ molecule ⁻² s ⁻¹)	Reference
43	I ₂ + O ₃ → IO + OIO → I + IO + O ₂	7.74 × 10 ⁻¹⁴ exp(-2888/T) × 0.5 ^b 7.74 × 10 ⁻¹⁴ exp(-2888/T) × 0.5 ^b	(Vikis and MacFarlane, 1985)
44	I ₂ → I + I	3.32 × 10 ⁻¹¹ exp(-7906/T)	(O'Neal and Benson, 1962b)
45	I ₂ O ₂ + O ₃ → I ₂ O ₃ + O ₂	5.0 × 10 ⁻¹⁶	(Gómez Martin et al., 2013)
46	I ₂ O ₂ → I + OIO	1.2 × 10 ⁻³	(Gómez Martin et al., 2013)
47	I ₂ O ₂ → IO + IO	4.0 × 10 ⁻²	(Sommariva et al., 2012)
48	I ₂ O ₃ + I ₂ O ₃ → I ₄ O ₆	1.40 × 10 ⁻¹²	(Gómez Martin et al., 2013)
49	I ₂ O ₃ + I ₂ O ₄ → I ₄ O ₇	2.70 × 10 ⁻¹¹	(Gómez Martin et al., 2013)
50	I ₂ O ₃ + I ₂ O ₅ → I ₄ O ₈	1.90 × 10 ⁻¹¹	(Gómez Martin et al., 2013)
51	I ₂ O ₃ + O ₃ → I ₂ O ₄ + O ₂	1.00 × 10 ⁻¹²	(Sommariva et al., 2012)
52	I ₂ O ₄ + I ₂ O ₄ → I ₄ O ₈	2.7 × 10 ⁻¹⁰	(Gómez Martin et al., 2013)
53	I ₂ O ₄ + I ₂ O ₅ → I ₄ O ₉	1.2 × 10 ⁻¹¹	(Gómez Martin et al., 2013)
54	I ₂ O ₄ + IO → I ₃ O ₅	1.5 × 10 ⁻¹¹	(Gómez Martin et al., 2013)
55	I ₂ O ₄ + O ₃ → I ₂ O ₅ + O ₂	1.0 × 10 ⁻¹²	(Sommariva et al., 2012)
56	I ₂ O ₄ + OIO → I ₃ O ₆	1.5 × 10 ⁻¹⁰	(Gómez Martin et al., 2013)
57	I ₂ O ₄ → OIO + OIO	1.20 × 10 ⁻²	(Gómez Martin et al., 2013)
58	I ₂ O ₅ + I ₂ O ₅ → I ₄ O ₁₀	7.0 × 10 ⁻¹¹	(Gómez Martin et al., 2013)
59	I ₂ O ₅ + OIO → I ₃ O ₇	1.0 × 10 ⁻¹³	(Gómez Martin et al., 2013)
60	I ₃ O ₅ → I ₂ O ₄ + IO	6.2 × 10 ⁴	(Gómez Martin et al., 2013)
61	I ₃ O ₆ → I ₂ O ₄ + OIO	3.5 × 10 ⁴	(Gómez Martin et al., 2013)
62	I ₃ O ₇ → I ₂ O ₅ + OIO	3.7 × 10 ⁷	(Gómez Martin et al., 2013)
63	I ₄ O ₁₀ → I ₂ O ₅ + I ₂ O ₅	1.9 × 10 ³	(Gómez Martin et al., 2013)

#	Reaction	Rate coefficient ^a (s ⁻¹) or (cm ³ molecule ⁻¹ s ⁻¹) or (cm ⁶ molecule ⁻² s ⁻¹)	Reference
64	I ₄ O ₆ → I ₂ O ₃ + I ₂ O ₃	7.5 × 10 ⁵	(Gómez Martin et al., 2013)
65	I ₄ O ₇ → I ₂ O ₃ + I ₂ O ₄	1.6 × 10 ⁴	(Gómez Martin et al., 2013)
66	I ₄ O ₉ → I ₂ O ₃ + I ₂ O ₅	2.8 × 10 ³	(Gómez Martin et al., 2013)
67	I ₄ O ₉ → I ₂ O ₄ + I ₂ O ₅	8.7	(Gómez Martin et al., 2013)
68	INO + INO → I ₂ + 2 NO	2.9 × 10 ⁻¹² exp(-1323/T)	(Basco and Hunt, 1978)
69	INO (+ M) → I + NO	5.83 × 10 ⁻¹³	(Basco and Hunt, 1978)
70	INO ₂ + INO ₂ → I ₂ + 2 NO ₂	4.70 × 10 ⁻¹³ exp(-1672/T)	(Gawler et al., 2003)
71	INO ₂ → I + NO ₂	9.93 × 10 ¹⁷ exp(-11865/T)	(McFiggans et al., 2010)
72	IO + H ₂ → HOI + H	1.1 × 10 ⁻²⁴ T ^{4.00} exp(-5270/T)	(Hammaecher et al., 2011)
73	IO + H ₂ O → HOI + OH	3.2 × 10 ⁻²⁷ T ^{4.54} exp(-7870/T)	(Hammaecher et al., 2011)
74	IO + OH → HO ₂ + I	1.0 × 10 ⁻¹⁰	(Bösch et al., 2003)
75	IO + HO ₂ → HOI + O ₂	1.40 × 10 ⁻¹¹ exp(540/T)	(Atkinson et al., 2007)
76	IO + IO → I ₂ + O ₂	5.40 × 10 ⁻¹¹ exp(180/T) × 0.05 ^c	(Atkinson et al., 2007)
	→ 2 I + O ₂	5.40 × 10 ⁻¹¹ exp(180/T) × 0.09 ^c	
	→ I + OIO	5.40 × 10 ⁻¹¹ exp(180/T) × 0.45 ^c	
	→ I ₂ O ₂	5.40 × 10 ⁻¹¹ exp(180/T) × 0.44 ^c	
77	IO + NO → I + NO ₂	7.15 × 10 ⁻¹² exp(299/T)	(Atkinson et al., 2007)
78	IO + NO ₂ (+ M) → IONO ₂ (+ M)	k ₀ = 7.70 × 10 ⁻³¹ (T/300) ⁻⁵ , k _∞ = 1.50 × 10 ⁻¹¹ , F _c = 0.4	(Daykin and Wine, 1990)
79	IO + NO ₃ → OIO + NO ₂	6.10 × 10 ⁻¹²	(Dillon et al., 2008)
80	IO + O(³ P) → I + O ₂	1.35 × 10 ⁻¹⁰	(Canosa-Mas et al., 1999)
81	IO + O ₃ → OIO + O ₂	3.60 × 10 ⁻¹⁶	(Dillon et al., 2006)
82	IO + O ₃ → I + 2 O ₂	1.20 × 10 ⁻¹⁵	(Larin et al., 1999)

#	Reaction	Rate coefficient ^a (s ⁻¹) or (cm ³ molecule ⁻¹ s ⁻¹) or (cm ⁶ molecule ⁻² s ⁻¹)	Reference
83	IO + OIO → I ₂ O ₃	1.15×10^{-10}	(Galvez et al., 2013)
84	IONO ₂ → IO + NO	$2.10 \times 10^{15} \exp(-13718/T)$	(Kaltsoyannis and Plane, 2008)
85	OIO + OH (+ M) → HOIO ₂ (+ M)	$k_0 = 1.50 \times 10^{-27} (T/300)^{-3.93}$, $k_\infty = 5.5 \times 10^{-10} \exp(46/T)$, $F_c = 0.3$	(Plane et al., 2006)
86	OIO + NO → IO + NO ₂	$7.60 \times 10^{-13} \exp(606/T)$	(Plane et al., 2006)
87	OIO + OIO → I ₂ O ₄	4.20×10^{-11}	(Galvez et al., 2013)
88	IO + CO → I + CO ₂	$1.49 \times 10^{-17} T^{1.77} \exp(-5703/T)$	(Khanniche et al., 2016b)
89	I ₂ O ₅ + H ₂ O → 2 HOIO ₂	$3.61 \times 10^{-22} T^{2.05} \exp(-3886/T)$	(Khanniche et al., 2016a)
90	HOI + NO ₃ → IO + HNO ₃	$2.70 \times 10^{-12} (300/T)^{2.66}$	(Saiz-Lopez et al., 2016)
91	2 HOIO ₂ → I ₂ O ₅ + H ₂ O	$6.73 \times 10^{-27} T^{2.90} \exp(-2948/T)$	(Khanniche et al., 2016a)
92	HOIO ₂ + OH → OIO ₂ + H ₂ O	$1.76 \times 10^{-22} T^{2.39} \exp(-421/T)$	(Khanniche et al., 2017)

^a Kinetic parameters for use in the Troe equation. ^b Branching ratio estimated. ^c Branching ratio from (Gómez Martin et al., 2013).

Appendix A.3: Organic iodine gas-phase photolysis mechanism

Reaction	J (s ⁻¹) ^a	Reference	IRACM reaction
1 CH ₂ I ₂ + hv → CH ₂ I + I	7.29 × 10 ⁻³ ^d	(Burkholder et al., 2015) ^b (Mössinger et al., 1998) ^b (Roehl et al., 1997) ^b	I2_CH4 + hv → I_MR + I
2 CH ₃ I + hv → CH ₃ + I	5.80 × 10 ⁻⁶ ^e	(Burkholder et al., 2015) ^b (Fahr et al., 1995) ^b (Rattigan et al., 1997) ^b (Jenkin et al., 1993) ^b (Roehl et al., 1997) ^b	I_CH4 + hv → MR + I
3 C ₂ H ₅ I + hv → C ₂ H ₅ + I	6.62 × 10 ⁻⁶ ^f	(Burkholder et al., 2015) ^b (Rattigan et al., 1997) ^b (Roehl et al., 1997) ^b	I_ETH + hv → ETHR + I
4 CH ₃ CHI ₂ + hv → products	2.66 × 10 ⁻³	(Burkholder et al., 2015) ^b (Schmitt and Comes, 1980) ^b	I2_ETH + hv → PROD
5 C ₃ H ₇ I + hv → C ₃ H ₇ + I	2.61 × 10 ⁻⁵ ^g	(Burkholder et al., 2015) ^b (Roehl et al., 1997) ^b	I_HC3 + hv → HC3R + I
6 t-C ₄ H ₉ I + hv → t-C ₄ H ₉ + I	1.88 × 10 ⁻⁶	(Burkholder et al., 2015) ^b (Phillips et al., 1992) ^b (Kim et al., 1997) ^c	I_HC3 + hv → HC3R + I

^a Peak value at midday: photolysis rates are calculated for clear sky, begin of August, latitude = 51°N. ^b Cross sections. ^c Quantum Yield. ^d Cross sections from (Roehl et al., 1997) between 205 nm and 215 nm, mean of the cross sections from (Roehl et al., 1997) and (Mössinger et al., 1998) between 220 nm and 380 nm, cross sections from (Mössinger et al., 1998) at 285 nm, evaluation data from (Burkholder et al., 2015). ^e Mean of the cross sections from (Jenkin et al., 1993), (Fahr et al., 1995), and (Roehl et al., 1997) between 210 and 230 nm, mean of the cross sections from (Jenkin et al., 1993), (Fahr et al., 1995), (Roehl et al., 1997), and (Rattigan et al., 1997) between 235 and 330 nm, mean of the cross sections from (Fahr et al., 1995), (Rattigan et al., 1997) and (Roehl et al., 1997) between 335 and 350 nm, cross sections from (Rattigan et al., 1997) between 355 and 365 nm, evaluation data from (Burkholder et al., 2015). ^f Cross sections from (Roehl et al., 1997) between 205 and 230 nm, mean of the cross sections from (Roehl et al., 1997) and (Rattigan et al., 1997) between 235 and 355 nm, evaluation data from (Burkholder et al., 2015). ^g Sum of the photolysis parameters from CH₂ICH₂CH₃ and CH₃CHICH₃.

Appendix A.4: Inorganic iodine gas-phase photolysis mechanism

#	Reaction	$J(s^{-1})^a$	Reference
1	$I_2 + h\nu \rightarrow I + I$	6.24×10^{-2}	(Burkholder et al., 2015) ^b (Saiz-Lopez et al., 2004) ^b (Brewer and Tellinghuisen, 1972) ^c
2	$HI + h\nu \rightarrow I + H$	8.20×10^{-6}	(Burkholder et al., 2015) ^b (Campuzano-Jost and Crowley, 1999) ^b (Martin and Willard, 1964) ^c
3	$HOI + h\nu \rightarrow I + OH$	$3.29 \times 10^{-4}^d$	(Burkholder et al., 2015) ^b (Bauer et al., 1998) ^{b,c} (Rowley et al., 1999) ^b
4	$INO + h\nu \rightarrow I + NO$	$2.76 \times 10^{-2}^e$	(Burkholder et al., 2015) ^b (Basco and Hunt, 1978) ^b (Forte et al., 1981) ^b (van den Bergh and Troe, 1976) ^b
5	$INO_2 + h\nu \rightarrow 0.5 I + 0.5 NO_2 + 0.5 IO + 0.5 NO$	1.20×10^{-2}	(Burkholder et al., 2015) ^b (Bröske, 2000) ^b
6	$IONO_2 + h\nu \rightarrow 0.5 I + 0.5 NO_3 + 0.5 IO + 0.5 NO_2$	9.63×10^{-3}	(Burkholder et al., 2015) ^b (Joseph et al., 2007) ^c (Mössinger et al., 2002) ^b
7	$I_2O_2 + h\nu \rightarrow I + OIO$	$1.92 \times 10^{-2}^f$	(Sherwen et al., 2016a) ^b
8	$I_2O_3 + h\nu \rightarrow IO + OIO$	$1.92 \times 10^{-2}^f$	(Sherwen et al., 2016a) ^b
9	$I_2O_4 + h\nu \rightarrow OIO + OIO$	$1.92 \times 10^{-2}^f$	(Sherwen et al., 2016a) ^b
10	$IO + h\nu \rightarrow I + O(^3P)$	3.21×10^{-2}	(Burkholder et al., 2015) ^b (Bloss et al., 2001) ^b (Harwood et al., 1997) ^b (Ingham et al., 2000) ^c
11	$OIO + h\nu \rightarrow I + O_2$	2.55×10^{-1}	(Burkholder et al., 2015) ^b (Bloss et al., 2001) ^b

^a Peak value at midday: photolysis rate are calculated for clear sky, begin of August, latitude = 51°N. ^b Cross sections. ^c Quantum yield. ^d Mean of the cross sections from (Bauer et al., 1998) and (Rowley et al., 1999), evaluation data from (Burkholder et al., 2015). ^e Mean of the cross sections from (Basco and Hunt, 1978) and (Forte et al., 1981) between 223 and 290 nm, cross sections from (Basco and Hunt, 1978) at 300, 310, 360 nm and between 370 and 400 nm, mean of the cross sections from (van den Bergh and Troe, 1976), (Basco and Hunt, 1978), and (Forte et al., 1981) for the cross sections greater than 400 nm, evaluation data from (Burkholder et al., 2015). ^f Cross sections estimated to be equal to those of $IONO_2$ with a quantum yield equal to 1.

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