REVIEW OF THE POTENTIAL SOURCES OF ORGANIC IODIDES IN A NPP CONTAINMENT DURING A SEVERE ACCIDENT AND REMAINING UNCERTAINTIES

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ABSTRACT

In case of a severe accident, organic iodides (RI) are one of the volatile iodine species that can be released in the environment thus possibly contributing to people contamination by inhalation. The formation and decomposition reactions of organic iodides have been identified and studied through various experimental programs whose objectives were to understand their behavior and develop phenomenological models able to predict their volatility. Four potential sources of RI formation have been identified: (1) the reactor coolant system (RCS), (2) the containment sump, (3) the paints in the containment and (4) the containment gaseous phase. A review of the knowledge, chemical mechanisms leading to RI formation and decomposition and the remaining uncertainties is performed in order to recommend remaining needed experimental investigations. It has been identified that significant uncertainties remain on RI formation in the gaseous phase through reaction of iodine with volatile organic compounds (VOC, like methane) and that additional data should be obtained to improve its modeling as it can be a significant RI source during days after the beginning of the accident.

1   INTRODUCTION

Organic iodides have been identified as one of the main contributor to the Source Term (ST) in case of a severe accident in a nuclear power plant (NPP) due to its high volatility and radio-toxicity (especially CH_3I that has been found to be the main organic iodides species [1, 2]) and also due to its limited retention in some filtered containment venting systems (FCVS) [3]. Inorganic forms of iodine (like I_2, HOI, HI, iodine oxides aerosols (IOx) and multicomponent iodide aerosols) can also contribute to iodine releases in the environment. Moreover, organic iodides are known to be poorly washed down by containment spray systems as they are less soluble [4, 5] than the inorganic species. They also have been identified as the main species persisting in the atmosphere after Chernobyl accident [6] which makes necessary the identification of its formation and decomposition chemical pathways in a damaged NPP in order to better quantify the RI amount that could be released in the environment. From literature data and modeling work, this article discusses the identified and potential RI formation and decomposition sources (1) in the reactor coolant system (RCS); (2) in the containment sump and (3) from the containment painted surfaces whose recent data, model and uncertainties led to envisage the homogeneous gaseous reaction between volatile organic compounds (VOC) and molecular iodine to play a significant influence on organic iodides formation and volatility and for which representative experimental data are needed.

2   ORGANIC IODIDES FORMATION IN THE RCS

Even though the four PHEBUS tests conditions [7-10] do not cover the whole conditions range of a reactor severe accident sequences, they have shown that no organic iodides entered the containment from the RCS in the short term ("short term" has to be considered in this paper as lower than ≈ 10 hours after the

beginning of fission products release) despite VOC can be transferred in significant amount in the RCS from the core, especially for reactors containing B_4C as absorber material, B_4C degradation leading to the formation of significant amount of methane (CH_4). Moreover, they haven't been identified as an iodine species that could enter the containment whereas iodine aerosols and inorganic iodine were [3], despite the significant methane concentration expected in the RCS hot leg. In fact, at such temperatures (T > 700°C), RI formation and stability is not likely in the RCS as (1) the residence time in the RCS is expected to be quite low (some seconds) and (2) CH_3I decomposes very quickly for T > 700°C [11, 12] (its half-life ($t_{1/2}$) is lower than 9 seconds for T > 700°C). In case higher molecular weight organic iodides are present in the RCS, they are expected to decompose even faster than CH_3I according to the estimations made in Table 1 (these estimations were made thanks to the kinetics parameters determined by Kodama and Choudhary [12, 13]).

If we extrapolate their determined kinetics to 700°C and above, organic iodides whose molecular weight is higher than methyl iodide are expected to be decomposed instantaneously in the RCS. The decomposition products were found to be gaseous HI, I°, I_2 and several VOCs so that if any organic iodide compounds may be present in the RCS hot leg, they would contribute to form gaseous inorganic iodine. For the RCS short term releases, unless RI residence time in the RCS is longer than some seconds, the amount of organic iodides expected to be released from the RCS hot leg in the containment is expected to be rather low and even insignificant.

Table 1: Temperature needed to decompose half of the initial amount of organic iodide (assuming an order one for the decomposition reaction of organic iodides) in one hour ($t_{1/2}$ = 1 hour) and estimated half-life ($t_{1/2}$) at different temperatures

Organic iodide	Formula	Estimated temperature corresponding to $t_{1/2}$ = 1 h	Estimated $t_{1/2}$ at 300°C (sec)	Estimated $t_{1/2}$ at 400°C (sec)	Estimated $t_{1/2}$ at 500°C (sec)	Reference and temperature validity range (°C)
Methyl iodide	CH_3I	393°C	$4.15.10^6$	2194	8	[12] $333 < T < 600$
Ethyl iodide	CH_3CH_2I	348°C	$1.29.10^5$	135	0.8	[13] $250 < T < 380$
Isopropyl iodide	$(CH_3)_2CHI$	286°C	1369	4	$6.0.10^{-2}$	
t-butyl iodide	$(CH_3)_3CI$	224°C	8.7	$3.0.10^{-2}$	$3.2.10^{-4}$	

For the long term (and delayed) RCS releases, the temperature of the RCS is expected to decrease. RCS aerosols deposits (like CsI or AgI) in the RCS were found to be partly unstable in presence of air and steam for 400°C < T_{RCS} < 750°C [14, 15]. Their thermal decomposition leads to the formation of gaseous I_2 (it is enhanced by the presence of irradiation [16]) that could react with VOC remaining in the RCS, leading to a potential release of RI in the containment (provided they are stable enough at such RCS temperatures and VOC remain in the RCS).

Table 1 indicates the estimation of the organic iodides half-life at 300, 400 and 500°C (sometimes an extrapolation out of the validity range of the data has been made but it remains reasonable as the temperature difference is only 20°C). It is observed that for T_{RCS} > ~ 500°C, even if organic iodides are formed in the RCS, they shouldn't reach the containment in significant amount as they are not stable enough ($t_{1/2}$ < 8 sec for CH_3I). For T_{RCS} < ~ 400°C, organic iodides produced in the RCS by delayed releases could increase the containment RI level as their half-life (especially for CH_3I) is much higher than the expected transit time in the RCS (some seconds).
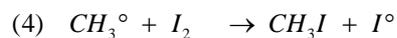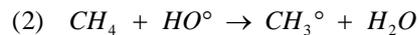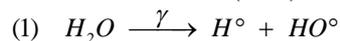
In the long term management of an accident, if (1) the RCS temperature is lowered down significantly (under 500°C) and (2) VOC react with deposited iodine aerosols and/or gaseous I_2 in the RCS (by a thermal and/or irradiation reaction), some RI delayed releases in the containment could be possible. An estimation (based on preliminary CsI and AgI kinetics decomposition data [14]) of the importance of this phenomenon for iodine ST is necessary at such RCS temperatures in order to establish whether more experimental data are needed.

3   ORGANIC IODIDES IN THE SUMP

3.1   Organic iodides formation

Organic compounds in the sump may arise from the transfer of gaseous VOC (from paint, cables, seals, oils and greases degradation) to the sump and organic compounds from immersed paint (paint degradation products and solvent releases). Various organic products were studied in various studies [17-19] like methane (CH_4), acetaldehyde (CH_3-CH-O), acetone (CH_3-CO-CH_3), acetic acid (HOOC-CH_3), methyl ethyl ketone (CH_3-CO-C_2H_5) and methyl isobutyl ketone ((CH_3)$_3$-C(OH)-CH_2-CH(OH)-CH_3).
Organic iodides formation in the sump is expected to occur mostly through chain reactions starting by water radiolytic dissociation into hydroxyl radical (HO°), followed by reactions involving dissolved VOC, molecular iodine (I_2) and hypoiodous acid (HOI) [20]. Two examples of chain mechanisms are given below for methane (CH_4) and acetic acid (HOOC-CH_3) [17, 21-23]:

(1) $H_2O \xrightarrow{\gamma} H° + HO°$

(2) $CH_4 + HO° \rightarrow CH_3° + H_2O$

(3) $CH_4 + I° \rightarrow CH_3I + H°$

(4) $CH_3° + I_2 \rightarrow CH_3I + I°$

(5) $CH_3° + HOI \rightarrow CH_3I + HO°$

(2') $HOOC-CH_3 + HO° \rightarrow HOOC-CH_2° + H_2O$

(3') $HOOC-CH_2° + I_2 \rightarrow HOOC-CH_2I + I°$

(4') $HOOC-CH_3 + I° \rightarrow HOOC-CH_2I + H°$

(5') $HOOC-CH_2° + HOI \rightarrow HOOC-CH_2I + HO°$

(6) $HOOC-CH_2I \rightarrow CH_3I + CO_2$

Another source of RI in the sump is the RI release from adsorbed I_2 on the immersed paint through a radiolytic process that remains to be quantified and identified.

From experimental data on organic iodides formation in the sump, a model was set up [24] and implemented in ASTEC code [25-27]. The half-life estimation from this model is not obvious as it depends on several parameters (dose rate, iodine and organics sump concentrations, temperature). A rough range estimation indicate that it can range from 0.5 hours to tens of hours.

3.2   Organic iodides decomposition

Even though RI are produced in the sump and can be transferred to the gaseous phase, they also undergo decomposition mechanisms below [28]:

(7) $CH_3I + H_2O \rightarrow CH_3OH + I^- + H^+$ (*dominant for pH* <11)

(8) $CH_3I + HO^- \rightarrow CH_3OH + I^-$ (*dominant for pH* >11)

The hydrolysis reaction is a non-reversible fast reaction ($t_{1/2} = 17$ min at 100°C and for pH < 11). For pH > 11, the reaction with hydroxyl ions (HO⁻) would dominate the hydrolysis reaction.

Another source of RI decomposition is the radiolysis for which several mechanisms have been identified below [29]:

(9) $e^-_{(aq)} + CH_3I \rightarrow °CH_3 + I^-$

(10) $H° + CH_3I \rightarrow °CH_3 + HI$

(11) $HO° + CH_3I \rightarrow °CH_3 + HOI$
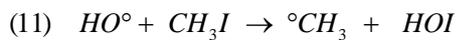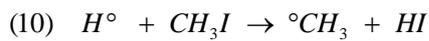
For these radiolytic reactions, CH₃I competes with O₂ to capture hydrated electrons (e⁻(aq)) and H° radicals. The kinetics of each reaction depends on the sump conditions (dose rate, dose, temperature and [CH₃I]). For a sump temperature higher than 80-90°C, CH₃I decomposition in the sump is expected to be fast (< 2.5 hours at 80°C and < 45 min at 90°C) [30] and controlled by the hydrolysis reaction.

RTF program [31] suggested that RI formation was mostly governed by reactions in the sump. In PHEBUS tests [7-10], the large excess of silver towards iodine in the sump for FPT0 and FPT1 (that contributed to quickly and efficiently trap I₂(liq)) and an alkaline pH for FPT2 (that makes I₂(liq) quickly disappear by hydrolysis [32-35]) tended to limit RI formation in the sump and their transfer to the gaseous phase so that phenomena in the containment atmosphere were the main sources of RI in these PHEBUS tests. The identified gaseous reactions are detailed and discussed in the following sections.

4   RI FORMATION FROM THE PAINTED SURFACES IN THE GASEOUS PHASE

Painted surfaces cover most of the building inner walls of PWR reactors for decontamination purposes and for preventing steel corrosion. Some studies were performed in order to choose the best paint chemical components that would ensure a high affinity towards volatile iodine (I₂, CH₃I and HI) without compromising paints adherence to the substrate and its mechanical properties [36, 37]. Amine groups were found to interact efficiently with the different forms of volatile iodine (as the trapping kinetics is quite fast and efficient). As a result, Epoxy type paints were defined as good candidates for most PWRs even though some reactors are covered with other type of paint (Zinc primer, polyurethane…). More recently a dedicated study on iodine/epoxy-paint interactions showed that the amine and amide functions as well as aromatic groups of the epoxy-paint structure are involved in donor-acceptor type interaction with iodine [38]. Nevertheless, despite the high affinity of Epoxy paint for volatile iodine, the high radiation field brought by the FP in accident situation can lead to a significant release of volatile organic iodides from the paints [32, 39, 40], suggesting that a significant part of the gaseous RI could come from the paint releases located in the gaseous phase of the containment building. It was also supported by the PHEBUS and ISTP programs results and interpretation [41-44]. A similar result was found in the framework of the ISTP and STEM programs thanks to EPICUR facility as no significant RI release from the sump was observed [45] whereas significant RI amount were observed to be released from Epoxy paint located in the gaseous phase [46]. Other studies also highlighted the need to better quantify the volatile RI contribution of the paint in the gaseous phase [47-49]. These releases needed to be quantified and modeled for severe accident code applications.

Most of these experimental studies (except in EPICUR facility) were performed in batch experiments for which the quantified volatile RI is the result of equilibrium of reactions happening in various media (sump, gaseous phase and surfaces). For the studies performed without sump and from which a model was set up [40, 50], authors assumed that the amount of gaseous RI corresponded to the RI release from the paint. However, the consideration of iodine oxides chemistry was not yet known and not considered in the models. The low amount of gaseous RI was thus resulting from a global balance between formation and decomposition mechanisms. As a result, the RI formation models from painted surfaces that were developed were implicitly considering IOx aerosols formation and decomposition (IOx influence on iodine volatility is now clearly established by recent studies [51]). Consequently, the corresponding models are valid for the vessel geometry and test conditions used to get the experimental data but the model application to other experiments and conditions generally doesn't allow a good simulation of these other data which suggests that one (or more) phenomenon is missing in the iodine chemistry modeling.

In order to avoid such a modeling flaw, specific reactions should be preferentially studied in a vessel whose atmosphere is quickly renewed and with on-line measurements so that kinetics models can be properly developed. This approach allows each phenomenon to be studied and modeled in a more relevant manner before applying the kinetics model to other conditions, to other vessels geometry or to plant applications.

EPICUR facility allows such kinetics quantification as the gaseous species have a low residence time in the irradiation vessel (usually under 20 min) which limits significant gaseous speciation modification before the species reach the selective Maypack filters (that traps I_2 and RI) [46]. RI release kinetics from painted surfaces were thus studied in EPICUR facility in representative conditions of a reactor accident through the OECD project STEM and its follow-up STEM2. Several parameters were varied like the temperature, humidity (RH), dose rate, and iodine adsorbed concentration on the paint and new results were obtained. It was found that the main RI (and I_2) gaseous releases take place only for a few irradiation hours (< 10-15 hours) before slowing down significantly for longer irradiation time for which both releases almost stop [46]. An example is given on Figure 1 on which the influence of the humidity is shown at 80°C. The uncertainty on the experimental data was estimated to be 30% for RI and 35% for I_2 [46].
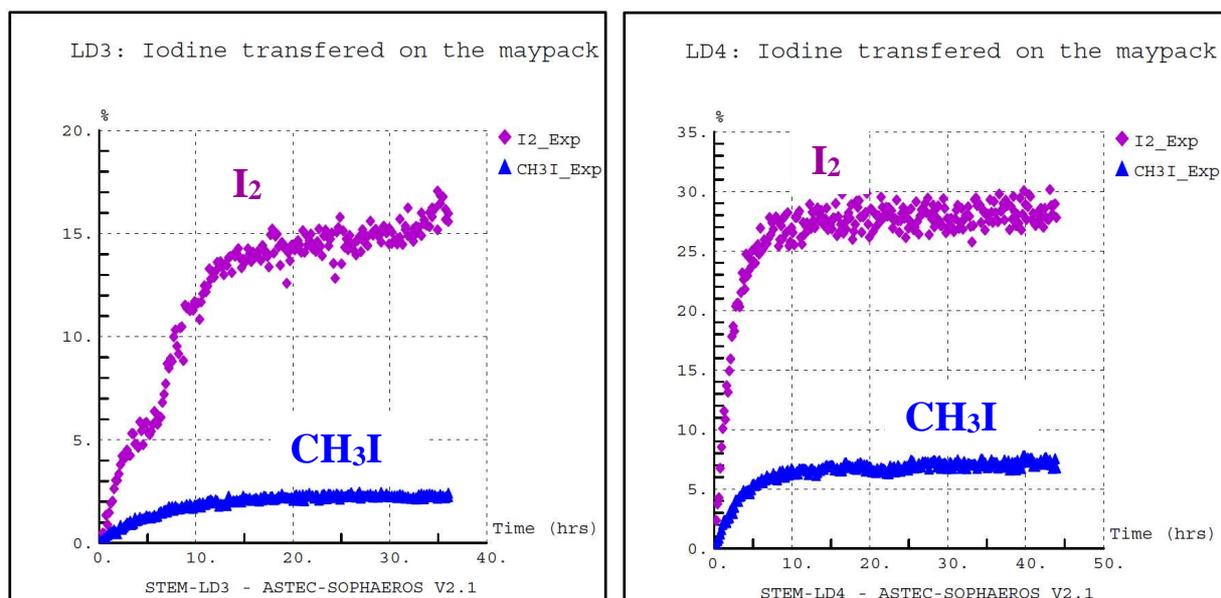

Figure 1. % of gaseous I_2 and RI release kinetics vs. time from a painted Epoxy coupon for STEM/LD3 (80°C, RH=60% and $[I]_{ads} = 9.0.10^{-5}$ mol.m^{-2}) and LD4 tests (80°C, RH=20% and $[I]_{ads} = 6.5.10^{-5}$ mol.m^{-2}) – Percentage refers to the initial iodine inventory adsorbed on the paint

A new kinetics model was set up for unaged Epoxy paints [46] and then applied to the analysis of the four PHEBUS tests in order to check whether the releases of RI and I_2 from the paint could explain the observed experimental gaseous RI and inorganic iodine PHEBUS containment concentrations. In order to complete the analysis, uncertainties of the iodine-paint model (and other reactions in ASTEC/SOPHAEROS) were estimated and propagation uncertainties calculations were performed to evaluate how the iodine-paint model uncertainties (estimated with a conservative approach) are influent on the modeling of gaseous RI in PHEBUS FPT-3 containment (for which almost 95% of the iodine entering the containment was identified as inorganic gaseous species which limits the uncertainties on boundary conditions in the calculation). It was looked at the 5% and 95% percentile that encapsulate 90% of the modeling results and also to the 50% percentile (intermediate curve) that has to be considered as the average curve.

The left part of Figure 2 shows the influence of the uncertainties propagation without activating the gaseous reaction. Despite models uncertainties have been estimated, the production of RI from paint releases could explain RI volatility only in the very short term (< 5 hours, before the maximum iodine concentration) whereas it is significantly underestimated from 5 hours to $\approx$ 60 hours even though the tendency is right. From 70 hours to the end of the test, the FPT3 data could be explain by the paint releases. Even if it is not possible to generalize this results to all scenarios cases, it seems that a significant RI formation pathway is missing during the first 2 days and needs to be added in order to reproduce the measured RI concentrations. As no significant iodine transfer from the sump to the gaseous phase was observed in the test and as the containment has been insulated quite early in the transient (at ~ 5 hours as opposed to the total test duration of $\approx$ 110 hours), the only way to get higher concentration of volatile iodine (RI and I_2) is to consider new phenomena that have to take place in the gaseous phase and/or on the steel surfaces of the vessel.
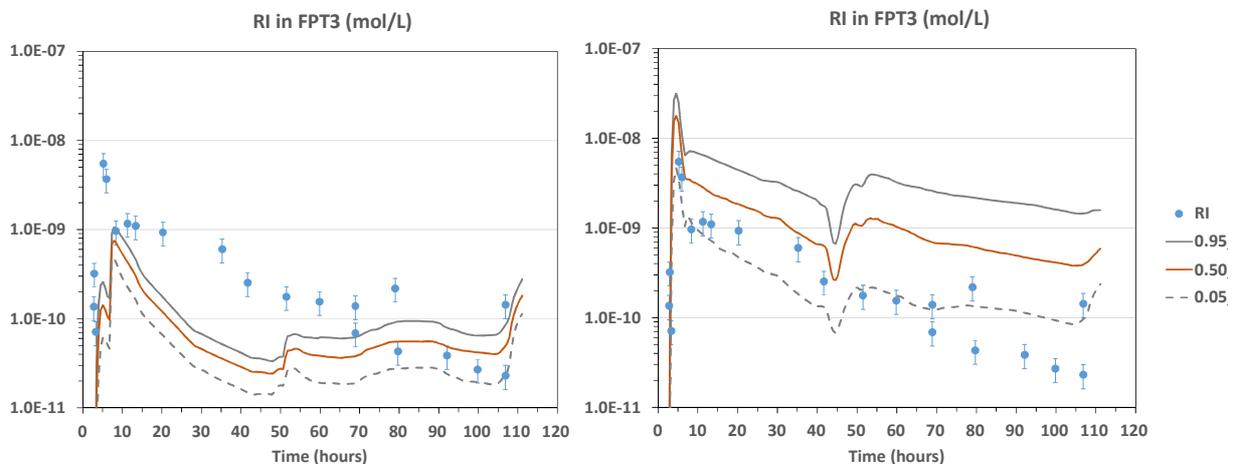

Figure 2. Comparison of measured and calculated gaseous iodides concentration for PHEBUS FPT-3 test considering (1) the iodine-paint model <u>only</u> (on the left, no gaseous reaction between VOC and I_2) or (2) the iodine-paint model <u>and</u> the gaseous radiolytic reaction between VOC and $I_{2(g)}$ (on the right) and their model uncertainties

Volatile organic compounds (VOC) are present in any facility, the minimum concentration being defined at least by the background concentration of methane in the atmosphere (~ 3.10^{-8} mol.L^{-1}). Higher VOC concentrations are expected in any reactor containment as the VOC sources are expected to be multiple: (1) polymer (paint, cables, seals, oils and greases) radiolytic degradation that promotes the release of VOC (especially at high temperatures that allow energetic barrier to be overcome), (2) B_4C control rods degradation that leads to significant amount of methane, carbon monoxide (CO) and carbon dioxide (CO_2)

[52] and (3) molten core concrete interaction (MCCI) also leading to CO and CO_2 release. Other organics can be present like oils, greases *etc.* Beahm showed that VOC containment concentration could increase by 3-4 orders of magnitude in 12 hours due organic material radiolysis which is consistent with the hydrocarbons concentration found in TMI-2 containment 13 months after the accident ($\sim 3.10^{-5}$ mol.L^{-1}) [52]. It thus raises the question if these VOC could react with $I_{2(g)}$ and lead to significant amount of volatile RI. This is discussed in the following section

5 RI FORMATION FROM HOMOGENEOUS REACTIONS IN THE GASEOUS PHASE

Two reactions types are referenced in the literature involving methane and gaseous molecular iodine: the thermal reaction and the radiolytic reaction whose influence on RI volatility is discussed below.
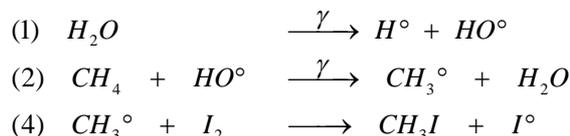Despite several open references published until the 1990' about this homogeneous reaction, it is not clear to us why the study of this potential gaseous RI production route was not considered for the past 20 years as the sump or the painted surfaces production were. This article gives us the opportunity to make a review on these gaseous processes.

5.1 Thermal reaction between methane and volatile I_2

The thermal reaction between methane and $I_{2(g)}$ has been debated in the literature several times. Nevertheless, it is not expected to play a significant influence at the containment temperatures (expected to be < 200°C) as the energetic barrier is high [53]. The temperature would need to increase up to 400-500°C to have a significant influence on RI formation kinetics. These high temperatures might be locally reached (by molten materials or hydrogen deflagration) but they are not expected to play a significant influence as (1) the volumes considered around molten materials are much smaller than the containment volume and (2) the time during which a deflagration would influence the gaseous temperature is expected to be rather small (some seconds). The thermal reaction is thus not expected to play a significant influence in the containment conditions during an accident.
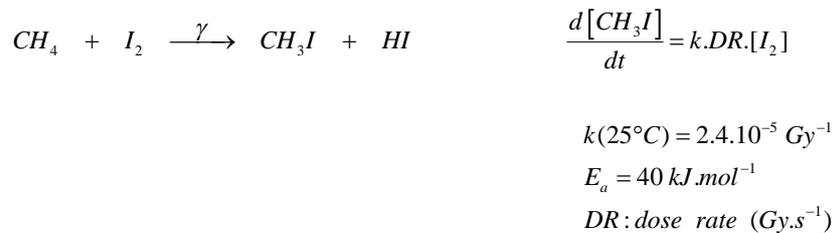
5.2 Radiolytic reaction between methane and volatile I_2

Even though it is well recognized and demonstrated that RI can be easily formed in the sump from the reaction between $I_{2(liq)}$ and organic radicals (R°) [19, 54, 55] and also in the gaseous phase in inert conditions (for some boiling reactors) [53, 56-58], some authors stated that the homogeneous gaseous phase reaction between methyl radical (°CH_3) and $I_{2(g)}$ is not likely because the concentration of both reactants is low and also because the presence of oxygen would scavenge quickly °CH_3 radicals before iodine could react with it [31, 59]. Nevertheless, other authors could observe a significant RI formation from a mixture of methane, air and iodine under irradiation [53, 56-58, 60] that is increased significantly when an inert gas is used instead of air (for some BWR case). The proposed mechanisms are the following ones:

$$(1) \quad H_2O \quad\quad\quad\quad \xrightarrow{\gamma} \quad H° \ + \ HO°$$

$$(2) \quad CH_4 \ + \ HO° \quad \xrightarrow{\gamma} \quad CH_3° \ + \ H_2O$$

$$(4) \quad CH_3° \ + \ I_2 \quad\quad \longrightarrow \quad CH_3I \ + \ I°$$

Bartonicek has published the most representative data. A few experiments were performed dealing with the irradiation of a mixture of methane, gaseous I_2 in air in a glass vessel whose conditions (temperature, dose rate and concentrations) are representative of those of a reactor building [58]. He also checked the influence of the temperature between 60°C and 100°C. From these data, he showed that CH$_3$I is quickly formed under irradiation and also quickly disappears in the gaseous phase (it is decomposed into IOx

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aerosols that settle down onto and diffuse onto the surfaces). The whole process takes less than 5 hours to be complete so that RI gaseous formation is expected to be rather fast under irradiation. CH_3I formation is found to be positively influenced by the rise of the temperature which is consistent with a previous study also performed under irradiation [61] (whose data were obtained in absence of oxygen though).

From these data, a preliminary radiolytic kinetics model was developed with the few data available with the objective to check whether this reaction could participate in a significant and relevant manner to the gaseous RI production in PHEBUS tests. The model is shown below:

$$CH_4 \; + \; I_2 \; \xrightarrow{\gamma} \; CH_3I \; + \; HI \qquad\qquad \frac{d[CH_3I]}{dt} = k.DR.[I_2]$$

$$k(25°C) = 2.4.10^{-5} \; Gy^{-1}$$
$$E_a = 40 \; kJ.mol^{-1}$$
$$DR : dose \; rate \; (Gy.s^{-1})$$

As methane concentration was an order of magnitude higher than I_2 concentration in Bartonicek's experiments, it is assumed that its concentration remains constant during the few hours of irradiation so that the kinetics model developed (and assumed to be of an order one on iodine) is only dependent on iodine concentration. For a typical dose rate close to 1 $Gy.s^{-1}$, the estimation of the half-life is $t_{1/2} = 40$ min at 80°C and $t_{1/2} = 10$ min at 120°C. It would be even lower for higher dose rates and temperatures which seems to indicate a fast gaseous reaction that might significantly influence the RI gaseous concentration, especially in PHEBUS tests.

Figure 2 (right part) shows the influence of this preliminary radiolytic reaction (and its uncertainty as a factor from 1 to 5 has been considered on the gaseous reaction rate) on RI formation for PHEBUS FPT3 test for which around 95% of the iodine entering the containment was under an inorganic gaseous form. Until ≈ 50 hours, calculated organic iodide concentrations are increased by one order of magnitude and models quite well the experimental data. For higher time transient, RI formation is overestimated. It could be due to parameters like the containment relative humidity that is modified at ≈ 50 hours and whose influence is not taken into account in the gaseous model presented above. It underlines how important this gaseous reaction could be for the estimation of organic iodide volatility as this calculation determines (in this particular case) the RI concentrations over 2 days following the iodine release from the fuel. Even if they are not shown in this paper, the modeling of FPT0, FPT1 and FPT2 (whatever the fraction of gaseous iodine entering into the containment whose evaluation is less certain because of the uncertainty that remains on gaseous iodine adsorption on the aerosol filtration stage of the Maypack) also leads to the same tendencies, which supports the relevance of this gaseous radiolytic reaction to explain the measured organic iodides concentrations. However, this simple model needs to be verified and completed as there were only a few experimental data to optimize the model parameters so that there is a significant uncertainty on the kinetics rate and activation energy. The influence of oxygen content has already been shown to be significant [53, 56-58] and need to be better considered as low O_2 contents are expected in containments where igniters and/or recombiners operate to reduce H_2 combustion risk and as some BWRs are inerted. Moreover, the influence of the methane concentration, iodine concentration and relative humidity also needs to be checked and considered in the model in case they are significantly influent. Finally, the available literature data in this area are limited to methane. Other relevant VOC (ketone, alcohol) could also be studied to evaluate possible reactivity difference between these different kinds of VOCs. A dedicated experimental program is thus needed to produce data in order to enhance the modeling of the related gaseous organic iodides formation process. This should contribute to improve iodine ST assessments as this process can be determinant for organic iodides volatility over the days following the iodine release from the fuel.

6   RI DECOMPOSITION IN THE GASEOUS PHASE

Gaseous CH_3I decomposition under irradiation has been firstly studied by Tang [62] and has shown that the reaction is pseudo-first order with respect to CH_3I for concentrations lower than $2.4.10^{-7}$ mol.L^{-1}.
More recent studies have shown that (1) the reaction is not temperature dependent, (2) C_2H_5I decomposition obeys to a similar kinetics than CH_3I and (3) low oxygen concentration leads to a higher decomposition rate as more electrons are available for reaction with RI [63]. Moreover, CH_3I decomposition is a quite fast process as for dose rates close to ~ 1 Gy.s^{-1}, $t_{1/2(CH3I)} \approx 30$ min [48] (another way for RI to disappear is to be adsorbed on paint for which $t_{1/2} \approx 3$ hours). The decomposition kinetics rates obtained in these different studies are consistent and do not differ significantly so that a mature kinetics model is set up in severe accident codes [27].

However, the CH_3I decomposition products were not clearly identified in these studies. Wikjord identified the decomposition products to be iodine oxides (amorphous I_2O_4 and I_4O_9 in dry conditions) in a corona discharge device (no gamma irradiation) [64]. IOx compounds decompose into crystalline I_2O_5 and gaseous I_2 if the temperature is higher than 75°C (I_2O_4 thermal decomposition) or 140°C (I_4O_9 thermal decomposition) [65]. In presence of humidity, these three iodine oxides compounds are transformed into another iodine oxides species (HI_3O_8).
Some studies were launched on IOx formation in the framework of PARIS program [66, 67] and more recently on IOx decomposition [51] (STEM (2010-2014) and STEM2 (2015-2019) programs) in order to complete the iodine phenomenology in the gaseous phase with a reliable IOx formation and decomposition kinetics model for severe accident simulation software.

A reliable modeling of gaseous RI will require a reliable modeling of IOx formation and decomposition processes. Investigations to complete the corresponding modeling are on-going.

7   CONCLUSIONS

A review of RI formation and decomposition reactions in severe accident conditions has been performed in order to identify the main formation routes. In the short term, no significant RI contribution is expected from the RCS as the residence time of the species is low which limits the formation and the temperature is high which favors the destruction. In the long term, delayed releases could be possible if the RCS temperature decrease significantly (T < 400-500°C) allowing thus possible I_2 revolatization which would be free for possible reaction with organics remaining in the circuit. The importance of the process should be further evaluated.
From our PHEBUS tests analysis and calculations dealing with models uncertainties propagation, we show that RI formation can occur through gaseous phase processes in the reactor containment. The main RI formation reactions are expected to happen through radiolytic processes involving (1) releases from paints in the short term and (2) gaseous reaction of inorganic iodine with volatile organic compounds (like methane or short chain volatile organic compounds) over the days following the iodine release from the fuel.
The paint contribution has been well studied in the OECD-BIP/BIP2/BIP3 and OECD-STEM/STEM2 projects and a reliable model is available in ASTEC code [25].

There is less knowledge about the contribution of the gaseous radiolytic reaction between inorganic iodine and VOC to the RI in-containment concentrations. VOC can be present in the gaseous phase in large excess towards iodine due to (1) the degradation of paint, cables, seals, oils, greases, (2) the B_4C control rods degradation (releasing CH_4, CO and CO_2) and (3) MCCI that also releases CO and CO_2. Moreover, depleted oxygen contents can be expected in containments in many accident situations (often resulting from measures to limit the H_2 combustion risk) which have been shown to favor the formation of gaseous RI by this reaction. Consequently, this reaction could be an important source of RI in the containment over

the days following the iodine release from the fuel because conditions in a severe accident are likely to favor it. Further experimental investigations are thus needed for this gaseous reaction in order to generate experimental data and develop a reliable kinetics model for ST and radiological consequences evaluations. The strategy deployed should be to investigate, under irradiation, the main kind of organic compounds (alkane, ketone, carboxylic acid etc.) with a unique representative per category i) to identify the most reactive leading to higher Org-I formation and next ii) to estimate for the most reactive organics a global radiolytic reaction rate with I_2 (including the influence of the main influent parameters like the temperature and humidity).

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