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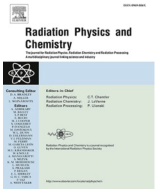

Radiolytic degradation of dimethyl telluride in aqueous solutions

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ABSTRACT

The formation of volatile radioactive species is a major concern in severe nuclear reactor accident scenarios. Release of radioactive material to the environment is highly governed by the volatility of the species and therefore it its crucial to understand the behavior of any such species during the accident and the days and weeks following. One of the volatile, yet highly understudied fission products is tellurium. Although tellurium has been released in significant amounts during the major nuclear accidents that have occurred, the knowledge of the behavior is still lacking. Here we present results on the radiolysis of dimethyl telluride, a highly volatile species shown to form in accident conditions. The behavior of dimethyl telluride was investigated under gamma irradiation in various aqueous solutions and conditions representative to severe nuclear reactor accident conditions. The results suggest that dimethyl telluride is relatively stable towards gamma irradiation and its degradation is highly affected by the amount of dissolved oxygen and competing species. It was found that dimethyl telluride degrades via oxidative processes by reacting with oxidizing radiolysis products e.g. •OH, $O^{\cdot -}$. In the absence of oxygen, several volatile telluride dimers were observed. The results presented here increase the interest in organic tellurides in severe accident conditions and highlight the need for further investigation of the re-volatilization and mitigation of volatile tellurium species.

1. Introduction

The two major nuclear accidents, Chernobyl and Fukushima, have demonstrated the severity of core meltdown and its consequences. This concern is not only limited to the early stage of the accident, but also to the following days, weeks and even years after the accident, where the stability of highly radioactive material inside the containment needs to be restored. Severe nuclear accident research focuses on the source term analysis of fission products which aims at providing information on the time and the amount of the releases. The research includes the behavior of fission products in the fuel, transport in the reactor coolant system and the reactions in the containment. The aim of severe accident research is to assess the potential release pathways and find ways to mitigate the releases to the environment during a severe accident.

One of the understudied radionuclides in severe accident research, especially in the containment conditions, is tellurium. Although, the released activities of tellurium isotopes from the major accidents are of same magnitude as cesium and iodine (Steinhauser et al., 2014; UNSCEAR, 2008) the attention received by tellurium is far from those of iodine and cesium. Furthermore, tellurium has been estimated to have been a major contributor to the dose to the public in the early stages after the Fukushima accident (Tagami et al., 2013). This is especially concerning since many of the released tellurium isotopes decay to iodine and therefore tellurium can indirectly contribute to the risk of thyroid cancer via its daughter nuclides (Shinkarev et al., 2015). But still, research relating to the tellurium source term is far from complete. Especially, the post-accident behavior of tellurium and the possible later stage releases are unknown.

Tellurium is released from the fuel after sufficient oxidation of the cladding (Collins et al., 1987) and transported through the reactor coolant system to the containment, mostly in a form of different aerosols (Espegren et al., 2021). The speciation of tellurium is highly dependent on the prevailing conditions, oxidizing or reducing (Beahm, 1987). Furthermore, the tellurium bearing aerosols are removed from the containment atmosphere and accumulate at the bottom of the containment including the sump (Kärkelä et al., 2021). The sump is a complex mixture of chemicals, the main components being a base for pH control and boric acid originating from the primary circuit or the emergency cooling systems. Moreover, the sump might contain dissolved insulation material, metals, and organic material, making it very hard to predict

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fission product behavior (NEA, 2013). There, tellurium can react with various other species including water radiolysis products, other fission products and organic material (McFarlane, 1996). Until recent years, tellurium was expected to mostly be present in its elemental insoluble form, and to not cause additional concern in the sump (Beahm, 1987; Laurie et al., 2013). However, novel results have shown that tellurium in its inorganic form can oxidize to a more soluble form in the containment sump conditions by reaction with water radiolysis products (Pasi et al., 2020). The dissolved tellurium is consequently capable to take part in further reactions in the sump. Of these reactions the interactions the reactions between inorganic tellurium and organic material are of interest. The formation of organic species is concerning due to their low boiling points and possible re-volatilization from the containment sump.

Although, tellurium and organic tellurides have not been expensively studied, the formation of organic iodides during a nuclear accident and especially methyl iodide, has been a concern for decades. Therefore, the formation (Beahm et al., 1987; Kim et al., 2018; Tietze et al., 2013) and degradation of methyl iodide (Buxton and Sims, 2003; Tang and Castleman, 1970) have been thoroughly investigated. However, the formation of volatile tellurium species has not been considered a concern in the past, and therefore they have barely received mention in severe accident literature (Beahm, 1987; Dickson and Glowa, 2019; Mcfarlane and Leblanc, 1996). However, due to the recent results showing the possible formation of organic tellurides from paint solvents, the need for further research is not disputable (Pasi et al., 2022). The formation itself is raising some concerns, however, the amount and stability of the formed species is yet unknown, and therefore the relevance of organic tellurides is still questionable. Since organic tellurides are not commonly used in aqueous solutions, their stability in water or other aqueous media is unclear. In addition, the high dose rates of ionizing radiation present in the sump, and its effect on the stability of any organic species present should be considered. In case organic tellurides are stable in aqueous solutions and under irradiation, there is a chance of re-volatilization from the sump to the containment atmosphere, and consequent increase in the activities released. Therefore, the aim of this work was to study the stability of dimethyl telluride in aqueous solutions representative to nuclear accident scenarios. The results provide important information on the relevance of organic tellurides and highlight the need for further research.

2. Background

In nuclear accident scenario, the ionizing radiation originates from the released fission products that accumulate in the containment atmosphere and to the sump. The dose rate in the containment is expected to be in a range of 1–10 kGy/h (Wren et al., 1999). The ionizing radiation can cause change in the speciation of fission products or degradation of e.g. organic material. These can consequently lead to the formation and destruction of volatile organic fission product species. These phenomena likely occur indirectly via reactions with water radiolysis products. The radiolysis of water produces a variety of oxidizing and reducing products, and the yield of the main products is presented in Reaction 1 (Buxton et al., 1988). The values in brackets indicate the G-values of the different species formed (μmol/J). In neutral water, the number of oxidizing and reducing species is relatively equal but this can be changed by changing the conditions e.g. adding different radical scavengers or changing the amount of dissolved oxygen in the system.

$$H_2O \rightarrow [0.28] \bullet OH + [0.07]H_2O_2 + [0.05]H_2 + [0.27]H_3O^+ + [0.27]e^-_{aq} + [0.06]H^\bullet \quad (1)$$

The radiation chemistry of organic tellurides is not well studied. However, there has been several studies done on the other organic chalcogens, sulfides (Bentley et al., 1972; Hatakeyama and Aklmoto, 1983; Yin et al., 1990) and selenides (Nishikida and Williams, 1975; Tobien et al., 2010; Wang and Tang, 2011), and their degradation using different advanced oxidation processes. In general, organic chalcogens are more susceptible to oxidation than reduction. Moreover, organic selenides have shown to be more stable than the sulfide analogs (Tobien et al., 2010). Due to the similarities in the behavior of the elements in the chalcogen group, analogous reactions can be expected for organic tellurides.

In the present study, the radiolysis of dimethyl telluride (DMT) in severe nuclear reactor conditions was investigated. To simulate these conditions, sodium thiosulfate and alkaline borate buffer were used as chemical additives. In addition, the effect of the amount of dissolved oxygen was investigated by either aerating or deaerating the aqueous solutions before the experiments.

3. Material and methods

3.1. Synthesis of $(CH_3)_2Te$

Method for dimethyl telluride synthesis was applied from (Kuhn et al., 1986). Elemental tellurium (15.1 g, Sigma Aldrich) was suspended in tetrahydrofuran (THF, 200 ml, Sigma Aldrich) under nitrogen atmosphere after which methyl lithium (MeLi, 75 ml, 1.6 M in diethyl ether, Sigma Aldrich) was slowly added. It was crucial to make the MeLi addition under N_2 since MeLi is extremely pyrophoric. The mixture was let to react for 30 min before methyl iodide (15 ml, Sigma Aldrich, >99%) was added. The solution was mixed overnight. After around 24 h, the precipitation was filtered and washed with THF and diethyl ether, dried and analyzed with ^{1}H-NMR (Varian 400 MHz) to characterize the intermediate Me_3TeI salt. Finally, dimethyl telluride, $(CH_3)_2Te$ was separated by mixing 10 g of Me_3TeI salt with triphenyl phosphene (15 g, Sigma Aldrich, 99%) and distilled under nitrogen at 120 °C. The product, a yellow oily solution, was then analyzed with GC-MS to determine the purity of DMT. The GC-MS analysis showed presence of a small amount of methyl-ethyl telluride. The amount was very low compared to the DMT yield but was still considered during the analysis of the results. The product was stored under nitrogen atmosphere to avoid oxidation or decomposition in air. The solutions used in the experiments were prepared fresh by taking a small volume of the DMT right before the experiments were conducted to minimize the exposure to air.

3.2. Solutions

The degradation of dimethyl telluride was investigated in four different conditions: aerated Milli-Q water (18MΩ·cm, Millipore), deaerated MQ water (N_2, 1 ppm O_2), alkaline borate solution (0.15 M NaOH, Emplura®, 99%, 0.23 M H_3BO_3, Merck >99.8%, pH 9.5) and sodium thiosulphate (0.06 M, Sigma Aldrich). The chemical solutions were chosen to represent those used in accident management. Borate buffer is a common matrix present in the containment sump whereas sodium thiosulfate has been used as an additive in the spray solution which also accumulates to the sump. In addition, both can affect the presence of water radiolysis species and therefore are interesting to use in this study. The concentrations of the chemical solutions were chosen to represent the conditions present in the liquid phases during a severe nuclear reactor accident. For each experiment, a stock of the respective solution was prepared by adding 400 μL of liquid DMT to 400 ml of solution and mixed. The equilibration time was kept relatively low to minimize decomposition of DMT before irradiation. The decomposition of DMT in the non-irradiated solutions in the time scale used was determined neglectable.

3.3. Irradiation

The samples were prepared by adding 10 ml of solution into 20 ml headspace glass vial, giving a gas to liquid ratio of 1:1. The solutions were then irradiated in the Gammacell 220 ^{60}Co source (MDS Nordion, Atomic Energy of Canada Ltd) giving a dose rate of 3.5 kGy/h. The dose rate applies well to severe accident conditions where the dose rate of the sump has been estimated to be between 1 and 10 kGy/h. The temperature in the Gammacell was around 300 K. Irradiation times ranged from 10 min to 6 h with a maximum dose delivered to the samples of 21 kGy except for the deaerated samples where the irradiation was continued to 28 kGy. The dose delivered to the samples was chosen after estimating a nearly total degradation of DMT in aerated water after preliminary experiments. Reference samples without irradiation were also prepared and analyzed. All samples were prepared in triplicates for statistical significance.

3.4. *Analysis techniques*

The samples were analyzed with gas chromatography mass spectrometer (GC-MS, Thermo Scientific) (5%-Phenyl)-methylpolysiloxane column) after they were taken out of the Gammacell. The GC-MS was used to analyze the degradation of DMT as well as identify any new volatile species forming during the irradiations. Although the GC-MS was not connected to the Gammacell, the time between taking out the sample and injection was kept short and as consistent as possible, and no effect originating from the slight delay in measurement was observed. The time between the end of irradiation and injection to the GC-MS was around 15 min. After the analysis of the volatile species, 1 ml samples were taken out to separate glass vials and oxidized with H_2O_2 to convert organic tellurides into inorganic soluble tellurium species for total tellurium concentration analysis by inductively coupled plasma mass spectrometer (ICP-MS, Thermo Scientific iCAP Q). The addition of H_2O_2 was done to avoid any loss of organic tellurides on the surfaces of the plastic vials used for ICP analyses. The total degradation by H_2O_2 was confirmed by GC-MS. The ICP-MS samples were diluted with HNO_3 (0.5 M Suprapur®, Supelco) to a suitable concentration. Also here, all samples were prepared in triplicates to give statistical significance to the analyses.

4. Results and discussion

4.1. *Concentrations*

To determine whether there was any loss of tellurium during the irradiations, the overall concentration was measured. The normalized results are presented in Fig. 1. As shown, the concentration stayed stable throughout the experiments in all four solutions. There are slight variations in the beginning which could be contributed to inhomogeneity of the stock solution which was prepared by adding dimethyl telluride to the saturation limit. Although the solution was mixed and let to settle before taking out the samples, it is possible that the concentration was slightly higher at the bottom of the stock solution since DMT sank to the bottom of the vial when the solution was prepared. The inhomogeneity of the solution resulted in maximum 20% lower concentration in the first samples compared to the rest of the irradiated samples where the concentrations stayed within approximately 8% range. The largest variation was measured in the alkaline borate solution samples whereas the most stable concentration was measured in the thiosulfate solution. However, no significant loss was observed during the irradiations and therefore, the change in the amount of DMT can be solely attributed to degradation and not any other process.

4.2. *Degradation of dimethyl telluride*

The GC-MS results for the degradation of DMT in the different aqueous solutions are presented in Fig. 2. The retention time of DMT in the column was around 2 min. As shown in the figure, the peaks decrease in intensity in the aerated solution (A) and in the borate buffer (B) with increasing radiation dose. The decrease seems to be more rapid in the beginning of the irradiation in the borate buffer compared to the aerated water. In the deaerated solution (C), the intensity stays relatively constant up to the dose of 7 kGy before any significant degradation occurs. The differences in the behavior suggest that the degradation is likely inhibited by the lack of oxygen in the system. Lastly, the degradation of DMT in the sodium thiosulfate seems to decrease rapidly in the beginning but then stay relatively constant. This behavior was quite unexpected and further investigated and discussed later.

The results from the GC measurements (Fig. 2.) were converted to normalized graphs for degradation of DMT as a function of irradiation dose (Fig. 3). In the aerated aqueous solution, dimethyl telluride decomposed under gamma irradiation, and after 21 kGy at a dose rate of 3.5 kGy/h, around 94% of DMT had degraded. The degradation as a function of dose had a decreasing exponential trend. A similar behavior was observed in the alkaline borate buffer solution. However, a slightly faster degradation was observed and nearly all DMT had decomposed after 21 kGy dose. In deareated solution, a different trend was observed. After 21 kGy dose only about 40% of DMT had degraded where in the presence of oxygen the value was 94%.

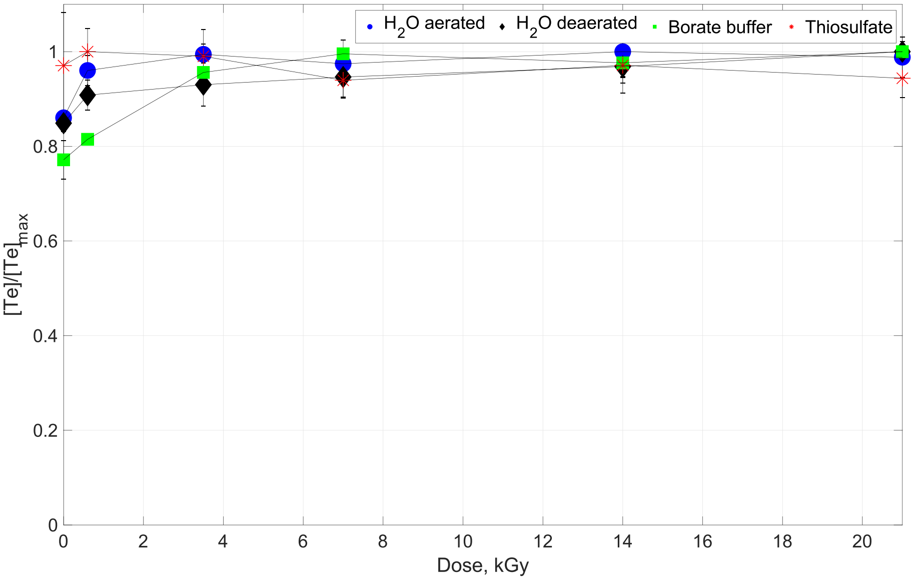

Fig. 1. Normalized total tellurium concentrations as a function of dose in various aqueous solutions.

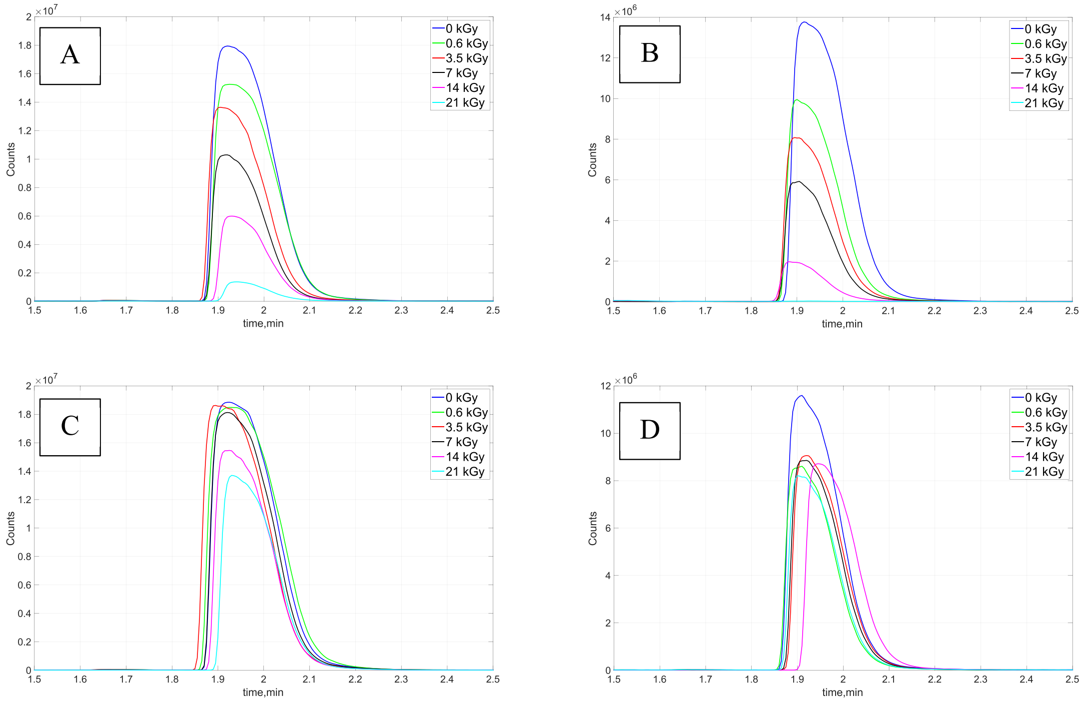

Fig. 2. Chromatograms for dimethyl telluride degradation in A. aerated aqueous and B. borate buffer C. deaerated aqueous D. sodium thiosulfate solutions.

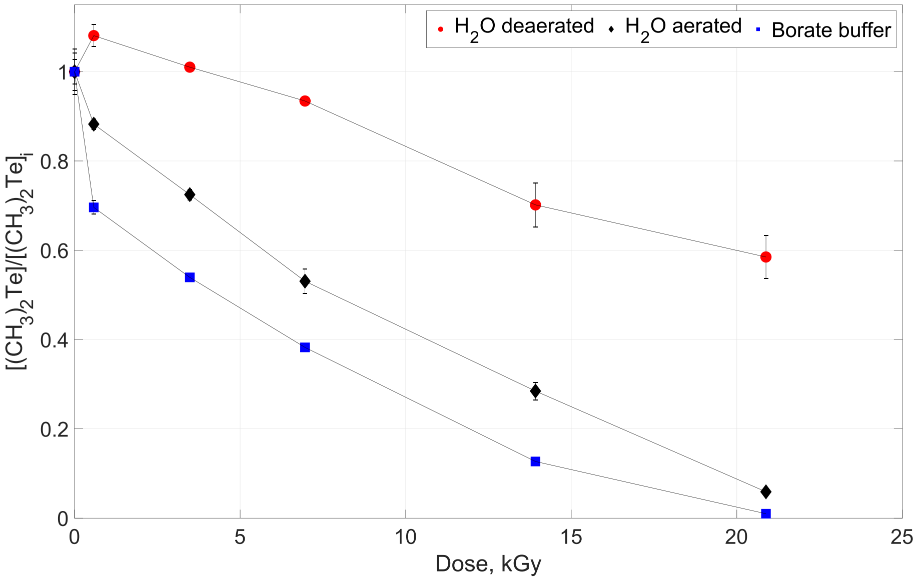

Fig. 3. Degradation of DMT in aerated (black) and dearated (red) water and alkaline borate buffer (blue).

The results for the aerated and deaerated aqueous solutions were plotted on a semi-log scale with log [DMT] as a function of time in seconds (Fig. 4). The concentration of DMT decreases exponentially with increased adsorbed dose in both solutions, suggesting first-order reaction kinetics. The slopes of the graphs in Fig. 4 give the first-order rate constants for the degradation of DMT. For the aerated and deaerated solutions the rates were $(1.2 \pm 0.1) \times 10^{-4}$ s^{-1} and $(2.8 \pm 0.3) \times 10^{-5}$ s^{-1}, respectively. The uncertainties represent the statistical errors. The rate in the presence of oxygen is significantly higher than the value in deaerated conditions. The presence of O_2 in the aqueous solutions leads to scavenging of reducing radicals to form $HO_2^{\bullet}$ and $O_2^{\bullet-}$ (Reactions 2 and 3). The rates for Reactions 2 and 3 are 1.9×10^{10} and 2.1×10^{10} L $mol^{-1}s^{-1}$, respectively (Buxton et al., 1988). The oxygen is also consumed via reactions with organic material which further decreases the dissolved oxygen concentration. The degradation of DMT in the two other matrices, borate and thiosulfate, were not plotted due to a more complex behavior and inaccurate the first-order fits. However, the factors and reactions likely affecting the degradation in these matrices are discussed.

$$e_{aq}^{-} + O_2 \rightarrow O_2^{\bullet -} \tag{2}$$

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet} \tag{3}$$

The most unexpected results were observed in the sodium thiosulfate solution (Fig. 5) There, DMT degraded rapidly within the first 10 min of irradiation to about 73% before stabilizing and only slightly

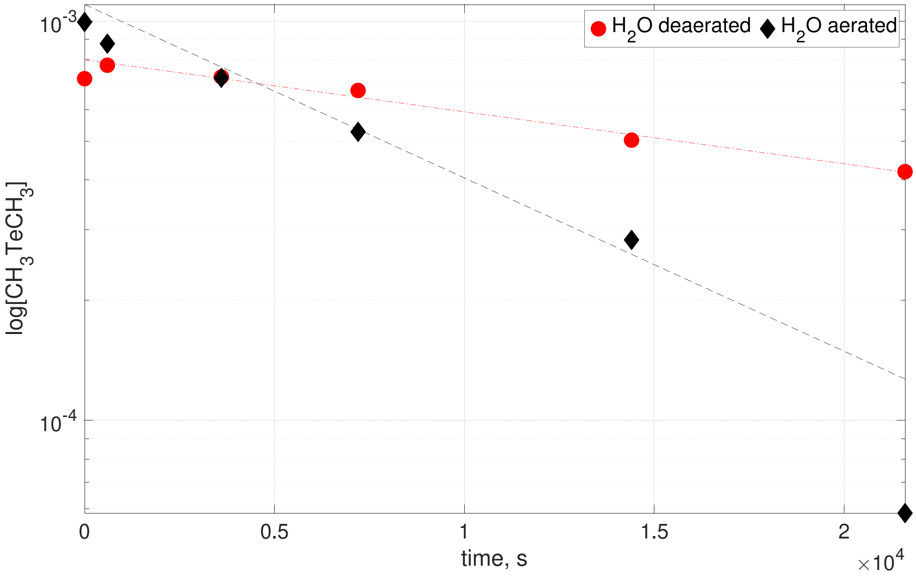

Fig. 4. The degradation of dimethyl telluride in aerated and deaerated solutions presented in first-order plots.

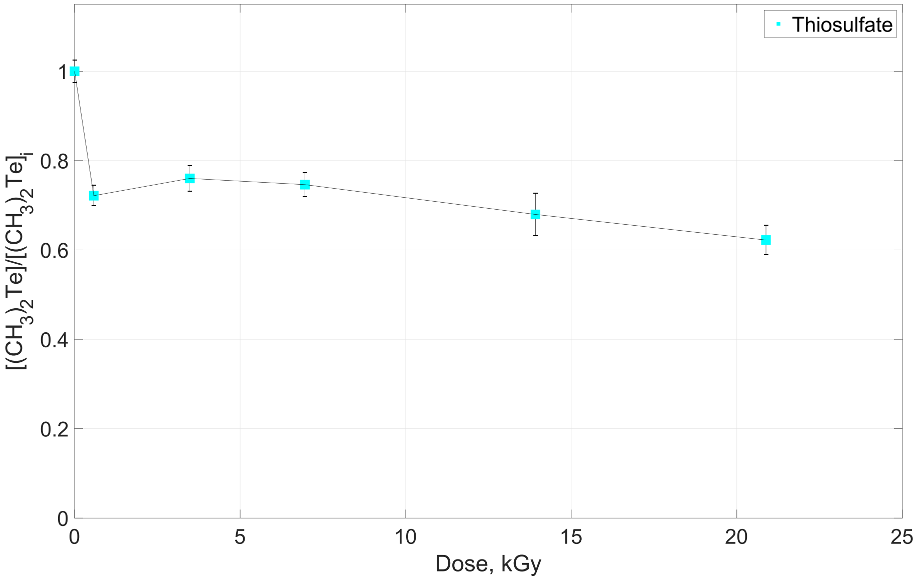

Fig. 5. Degradation of DMT in aqueous sodium thiosulfate. The line presented is not a fit but a connection between the data points.

decomposing during the rest of the irradiation. At the end, after 21 kGy, only about 40% of DMT had degraded. This behavior was unexpected, but likely relates to the complex radiolysis and scavenging behavior of thiosulfate discussed later.

The G-values for DMT degradation in the different solutions were calculated using the graphs in Fig. 3. The G-values are given are for the initial rate of each system. The G-values are given as μmol/J and presented in Table 1. The effect of oxygen can also be observed in the G-values since the values for the borate buffer and aerated aqueous are of same magnitude but in the daerated aqueous solution, the G-value is around 10 times lower. The G-values decrease in the order borate buffer, aerated and deaerated aqueous. Due to the unexpected and deviating results obtained in the thiosulfate solution, no confident information on the G-value can be presented.

Table 1
The G-values of dimethyl telluride degradation in different aqueous solutions.

	H_2O_{air}	$H_2O_{deaerated}$	$B(OH)_4$
G-value (μmol/J)	0.202	0.015	0.287

4.3. *DMT dimerization*

The GC-MS analysis showed new species forming with increased radiation dose in the samples prepared under nitrogen atmosphere. No new species were observed in the other solutions or conditions. The chromatograms and the corresponding mass spectra are presented in Fig. 6A and 6B. Fig. 6A Does not show the dimethyl telluride peak at around 2 min due to its abundance compared to the new formed species. However, the mass spectrum for DMT is shown as a reference and to show the dimerization in relation to the initial DMT spectrum. As shown, a peak at around 3 min increased in intensity with increasing radiation dose. The corresponding mass spectrum A was used to identify this as methyl-ethyl telluride, $CH_3TeCH_2CH_3$, with a mass ion at 174 m/z. Compared to the reference, where a small amount was present, the intensity after 28 kGy is over 9 times higher.

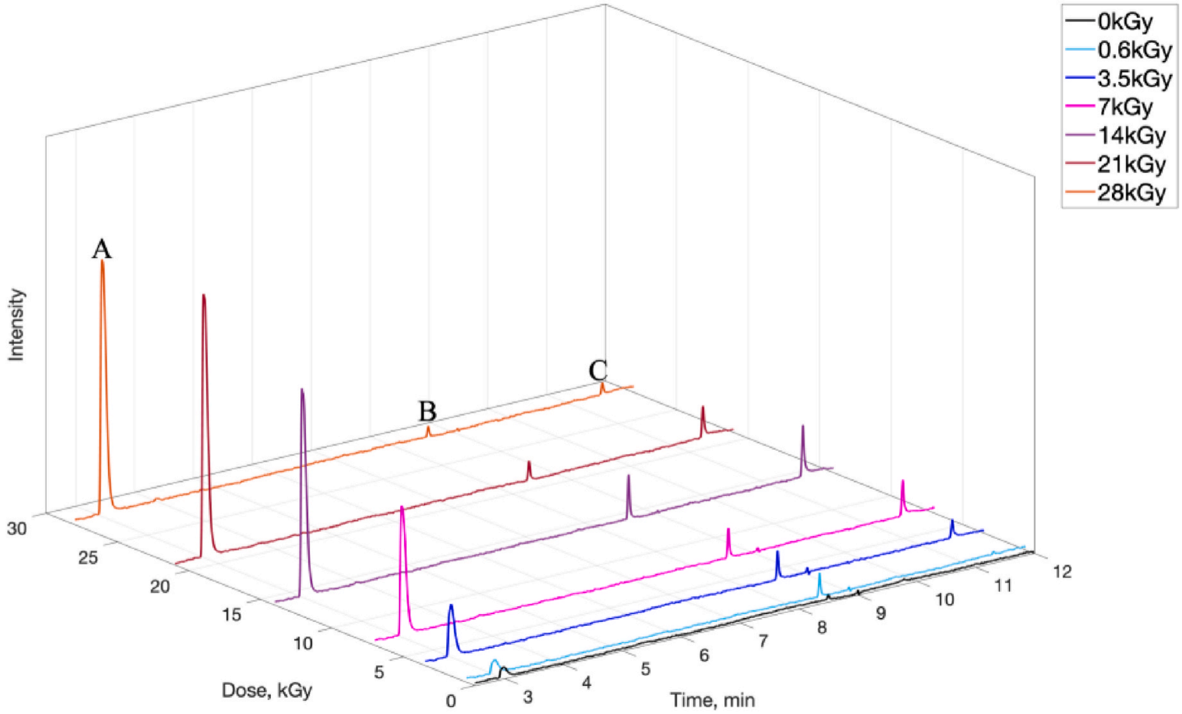

Fig. 6.A. The chromatograms of the irradiated dimethyl telluride solutions in deaerated conditions with increasing radiation dose. The letters refer to the new species observed during the irradiation. The corresponding mass spectra are presented in Fig. 5B.

Another peak was detected at around 3.8 min. This peak appeared after 21 kGy dose and slightly increased in intensity with increased dose. The corresponding mass spectrum B shows further lengthening of the carbon chain with a mass ion at m/z 188. This is likely attributed to the formation of methyl propyl telluride, $CH_3TeCH_2CH_2CH_3$. This is supported by the fractionation in the spectrum where the signals for dimethyl telluride are very low, almost non-existent, and instead there are high signals at around m/z 130 for Te, 143 for CH_3Te and 188 for $CH_3TeCH_2CH_2CH_3$.

In addition to the lengthening of the carbon chain, dimerization of DMT was also observed. At around 8.5 min, a peak was observed and identified by its mass spectrum C as dimethyl ditelluride, $CH_3TeTeCH_3$. The mass spectrum shows the methyl telluride fractions at around 130 (Te fractions) and 143 (CH_3Te). The signals for $(CH_3)_2Te$ are missing in the spectrum due to the dimer only having Te–CH_3 and Te–Te bonds. Lastly, another dimer was detected at around 11.5 min denoted as compound D. The mass spectrum D shows a complete fractionation for DMT between m/z 126 and 160 and the dimerization with m/z fractions between 250 and 300. The mass ion with m/z 300 corresponds to a dimer $(CH_3)_2TeTe(CH_3)$. The structure otherwise resembles that of dimethyl ditelluride dimer, $(CH_3)_2TeTe(CH_3)_2$, however, the mass spectrum only shows signals for three methyl groups attached. The amount of both high m/z dimers increase up to 14 kGy and start decreasing with higher doses. This is likely due to degradation by radiolysis products.

5. Proposed radiolysis reactions for dimethyl telluride

5.1. Aerated aqueous solution

Due to the efficient degradation of DMT in the aerated solutions, it can be assumed that the degradation occurs via oxidation reaction. This is supported by the fact that other organic chalcogens also degrade in a similar manner. There are several possible reactions that lead to the decomposition, all with the hydroxyl radical, •OH. Reaction 4 shows the attachment of the OH radical whereas Reaction 5 shows the elimination of a hydrogen to form a DMT radical and water. The last of these reactions is substitution of methyl group by the hydroxyl radical (Reaction 6). The rate constant for OH addition for dimethyl selenide is 2.1×10^{10} M^{-1} s^{-1} which can be used to indicate the rate of reaction for dimethyl telluride. All of these are possible pathways for the DMT degradation; however, we were not able to analyze these intermediates and could not identify any of these in the samples due to their short-lived nature. Therefore, the suggestions are solely assumptions but supported by previous research on radiolysis of organic chalcogens where both dimethyl selenide and dimethyl sulfide have been found to react in this manner (Hatakeyama and Aklmoto, 1983; Tobien et al., 2010)

$$CH_3TeCH_3 + \bullet OH \rightarrow (CH_3Te(OH)CH_3)^{\bullet} \tag{4}$$

$$CH_3TeCH_3 + \bullet OH \rightarrow (CH_3TeCH_2)^{\bullet} + H_2O \tag{5}$$

$$CH_3TeCH_3 + \bullet OH \rightarrow CH_3Te(OH) + CH_3 \tag{6}$$

The formed OH adduct (Reaction 4) can be further oxidized in the presence of oxygen to form CH_3TeOCH_3 radical (Reaction 7). With a further addition of a hydroxyl radical leads to an elimination of one of the methyl groups (Reaction 8).

$$(CH_3Te(OH)CH_3)^{\bullet} \overset{O_2}{\rightarrow} (CH_3TeOCH_3)^{\cdot} + HO_2 \tag{7}$$

$$(CH_3TeOCH_3)^{\cdot} \overset{OH}{\rightarrow} (CH_3TeO(OH)CH_3)^{\cdot} \rightarrow CH_3TeO(OH) + \bullet CH_3 \tag{8}$$

Another plausible reaction pathway presented for other organic chalcogens and therefore also expected for DMT degradation is the reaction with the oxygen radical $O^{\cdot -}$, a conjugate base for OH. The reaction is similar to that presented in Reaction 4 but with the addition of $O^{\cdot -}$ to the tellurium center atom yielding a telluroxide radical (Reaction 9). This reaction is analogous as presented for dimethyl selenide with a rate constant of 8.8×10^{9} M^{-1} s^{-1}. The reactions are affected by pH with Reaction 9 being the more dominant in pH over 10 whereas in lower pH the a protonation-deprotonation can also occur between the OH adduct and the conjugate base as presented in Reaction 10. In the DMT experiments, the borate buffer had a pH around 10 and therefore, Reaction 9

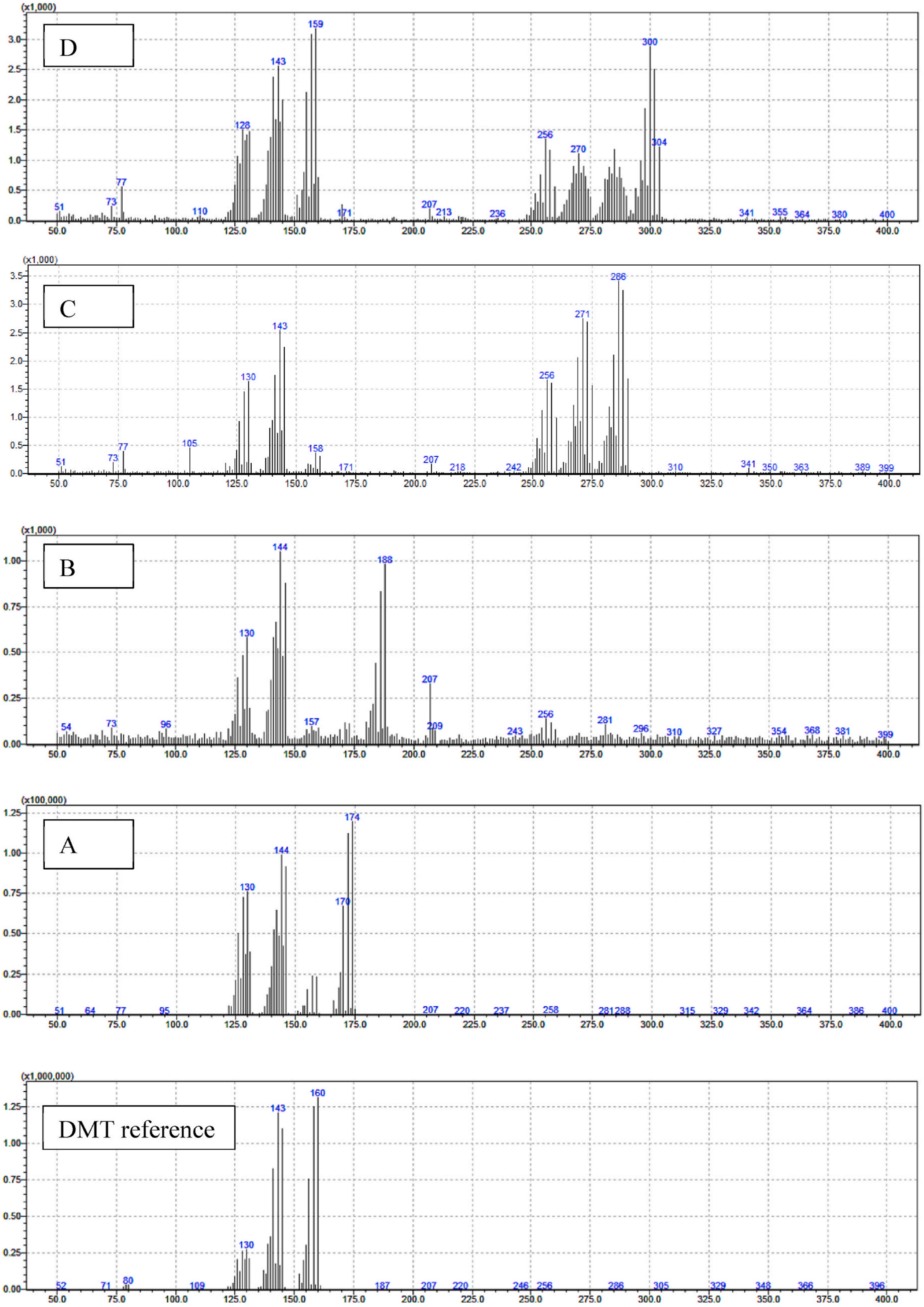

Fig. 6.B. The corresponding mass spectra: A. methyl ethyl telluride, B. methyl propyl telluride, C. dimethyl ditelluride D. dimethyl ditelluride dimer. The mass spectrum on the bottom shows the original dimethyl telluride.

could contribute to the higher degradation rate in the beginning compared to the neutral aqueous solutions.

$$CH_3TeCH_3 + O^{\cdot -} \rightarrow CH_3Te(O^{\cdot -})CH_3 \tag{9}$$

$$\left(CH_3Te(OH)CH_3\right)^{\bullet} + OH^{-} \leftrightarrow CH_3Te(O^{\cdot -})CH_3 + H_2O \tag{10}$$

5.2. *Effect of boric acid*

In the aerated alkaline borate solution, in addition to the oxygen radical and pH effect (Reaction 9), oxygen scavenging the reducing radicals (Reactions 2 and 3), boric acid has also been found to react with the solvated electron and hydrogen radical quite efficiently. The rate for Reaction 12 has been determined to be 3×10^6 M^{-1} s^{-1}. Previous research on radiolysis of boric acid has shown that hydrogen production resulting from Reactions 11 and 12 is rapid in the beginning of the irradiation before plateauing (Koike et al., 1969). In the DMT experiments a concentration of 0.23 M of boric acid was used in the solution, which corresponds to the concentration present in nuclear accident conditions. The relatively high concentration of boric acid increases its likely effect on the distribution of the water radiolysis products and consequently the rate of DMT degradation. The contribution could come from the scavenging of the reducing radicals (Reaction 11 and 12) and the consequent lesser effect of Reaction 2 and 3 enabling higher degree of oxidative decomposition of DMT.

$$H_3BO_3 + H\bullet \rightarrow H_2BO_3 + H_2 \tag{11}$$

$$H_3BO_3 + e^{-}_{aq} \rightarrow H_2BO_3^{-} + H \tag{12}$$

5.3. *Deaerated aqueous solution*

In the deaerated water, the degradation of DMT was significantly slower. The absence of oxygen results in the decrease in the oxidative decomposition and rather dimerization of dimethyl telluride into new species. In addition, Reaction 2 and 3 do not occur to the same extent in deaerated water and therefore the hydrated electron and hydrogen radical can be considered in the reaction pathways. Reaction 13 presents the dissociation of a methyl group via anionic radical intermediate. Similar dissociation can occur via reaction with hydrogen radical producing methyl tellurol and a free methyl radical (Reaction 14). Again, analogous reaction of other dimethyl chalcogens exist. Rate for the reaction of dimethyl selenide with the solvated electron is reported at 2.1 $\times 10^8$ M^{-1} s^{-1} and with hydrogen radical at 4.1×10^9 M^{-1} s^{-1} (Tobien et al., 2010). Similar values for the rate can be expected for dimethyl telluride.

$$CH_3TeCH_3 + e^{-}_{aq} \rightarrow (CH_3TeCH_3)^{\bullet -} \rightarrow CH_3Te^{-} + \bullet CH_3 \tag{13}$$

$$CH_3TeCH_3 + H^{\cdot} \rightarrow (CH_3TeHCH_3)^{\bullet} \rightarrow CH_3TeH + \bullet CH_3 \tag{14}$$

One of the new species was identified as methyl ethyl telluride which is suggested to form via Reaction 15 where a free methyl group formed from Reaction 13 or 14 attaches to the radical formed in Reaction 5.

$$(CH_3TeCH_2)^{\bullet} + \bullet CH_3 \rightarrow CH_3TeCH_2CH_3 \tag{15}$$

Further lengthening of the carbon chain to form the methyl propyl telluride detected in the deaerated samples is likely formed via similar reaction but instead of dimethyl telluride, this forms later after around 21 kGy dose indicating that it possibly forms from the methyl ethyl telluride.

$$CH_3TeCH_2CH_3 + \bullet OH \rightarrow (CH_3TeCH_2CH_2)^{\bullet} + H_2O \tag{16}$$

$$(CH_3TeCH_2CH_2)^{\bullet} + \bullet CH_3 \rightarrow CH_3TeCH_2CH_2CH_3 \tag{17}$$

The other new species were telluride dimers where a bond between two tellurium atoms was formed. The first of these species was identified as dimethyl ditelluride. The suggested pathway includes a product from the substitution reaction of one methyl group with OH (Reaction 6) and the product from Reaction 14 following the dimerization (Reaction 18). This reaction is analogous to that for the formation of dimethyl disulfide (Bonifačić et al., 1975) and therefore can be also considered plausible for dimethyl ditelluride.

$$CH_3Te(OH) + CH_3TeH \rightarrow CH_3TeTeCH_3 + H_2O \tag{18}$$

The species with the highest mass, a dimethyl ditelluride dimer, was also analyzed from the GC results. This species likely forms via initial addition of either OH or O^{-} radical (Reaction 4 and 9) following its substitution with another DMT molecule (Reaction 19 or 20). The formed dimer likely has a similar 3-electron bond structure as its analog dimethyl diselenide (Tobien et al., 2010) and dimethyl disulfide dimers (Göbl et al., 1984). As mentioned, no intermediate species were observed, only the final species and therefore we cannot fully confirm the reaction pathways.

$$(CH_3Te(OH)CH_3\ )^{\bullet} + CH_3TeCH_3 \rightarrow \left((CH_3)_2Te.\because.Te(CH_3)_2{}^{+} + OH^{-}\right. \tag{19}$$

$$CH_3Te(O^{\cdot -})CH_3 + CH_3TeCH_3 + H_2O \rightarrow \left(\ (CH_3)_2Te.\because.Te(CH_3)_2\ \right)^{+} + 2\ OH^{-} \tag{20}$$

This type of dimerization in the absence of oxygen has been observed with other organic compounds. Methyl ethyl ketone for example has been found to go through similar processes where it is decomposed by oxidizing radicals in aerated aqueous solution but forms various dimers in the absence of oxygen (Glowa et al., 2000). In addition, both dimethyl selenide and dimethyl sulfide have been found to form similar dimers when exposed to gamma irradiation (Meissner et al., 1967; Nishikida and Williams, 1975). These findings support the results presented here and further strengthen the assumption that the DMT degradation is an oxidative in nature.

5.4. *Effect of thiosulfate*

The degradation of DMT in the aqueous sodium thiosulfate (TS) showed an interesting trend where the degradation was very rapid in the early stage of the irradiation and then stabilized. Although, literature does not present any analogous organic chalcogen reactions, similar behavior of TS enhancing degradation of organic material has been observed for other various organic species (Yang et al., 2020; W. W. Zhang et al., 2021; Z. Z. Zhang et al., 2021). To explain the results, the thiosulfate behavior needs to be discussed. The radiation chemistry of thiosulfate (TS) is very complex especially in aerated solutions. In these experiments, we were again not able to analyze the intermediate radical species of TS and only observed the overall oxidation from TS to sulfate. However, since TS can form very reactive radical species especially in the presence of oxygen, we suggest that these would explain the rapid degradation in the early period of the irradiation. This is likely attributed to the formation of sulfate radical, $SO_4\bullet^{-}$. First step of the reaction is the formation of either TS or sulfite radical (Reations 21 and 22) (Glebov et al., 2022). In the presence of oxygen, $SO_3\bullet^{-}$ can form peroxomonosulfate radical anion $SO_5\bullet^{-}$ (Reaction 23). These radicals can then recombine to form $SO_4\bullet^{-}$ (Reaction 24 (Herrmann et al., 1995)) which can then oxidize DMT and cause the rapid degradation. Although this could explain the rapid decrease in the beginning of the irradiation, the stabilization following is yet unclear and would require further experiments to be fully explained.

$$S_2O_3^{2-} + O_2 \xrightarrow{\gamma} S_2O_3^{\bullet -} + O_2^{\bullet -} \tag{21}$$

$$S_2O_3^{2-} + O_2 \xrightarrow{\gamma} SO_3^{\bullet -} + SO_2^{\bullet -} \tag{22}$$

$$SO_3^{\bullet -} + O_2 \xrightarrow{\gamma} SO_5^{\bullet -} \tag{23}$$

$$SO_5^{\bullet -} + SO_5^{\bullet -} \xrightarrow{\gamma} 2SO_4^{\bullet -} + O_2 \tag{24}$$

6. Conclusion

The degradation of dimethyl telluride was studied under gamma irradiation in various aqueous solutions. The aim was to investigate whether organic tellurides should be considered a concern in nuclear reactor accident conditions. As previous research has shown, organic tellurides can form in the sump solution during a nuclear accident, however, the stability of the formed species has been unclear. The results presented here show that dimethyl telluride is relatively stable in aqueous solutions. The rate of degradation follows first-order kinetics and is dependent on the amount of dissolved oxygen available and the presence of competing species. It was shown that the degradation occurs via oxidation reaction as it does for analogous organic chalcogens. In the absence of oxygen, the degradation was significantly slower and instead dimerization reactions occurred forming new volatile telluride species. The results show that due to the relative stability organic tellurides should be further investigated in severe nuclear accident context and the re-volatilization and mitigation of these species should be considered in future research.

Author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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