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Behavior of Iodine under Gamma Irradiation Condition

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1. Introduction

The behavior of radioactive iodine species has been subjected to many studies because the radionuclides determine the total air radioactivity around an accident area during the first several weeks after an occurrence of a severe accident in nuclear power plant. In particular, because the oxidized species I_2 is highly volatile and can be an important source material of organic iodide, many studies on the gamma oxidation of I^- and the formation of organic iodide have been carried out. In our group, we have investigated the effects of the gamma dose, irradiation time, concentration of chemical species, and pH of the solution on the formation of I_2 and CH_3I for last several years. In this paper, we summarized our results [1-8] on the formation of I_2 and CH_3I, and extracted the reaction rate data related to the volatility of iodine from the results [2,4,8]. And then, using a simple iodine behavior model, we tried to evaluate the behavior of iodine under gamma irradiation conditions.

2. Methods and Results

In this section some of the gamma irradiation facility, chemical measurement system, experimental conditions, and results are described.

2.1 Experimental Method

Gamma irradiation was provided by ^{60}Co sources and the irradiation system was manufactured by MDS Nordion, Canada. The gamma dose rate was controlled in the range of 1-10 kGy h^{-1}. The gamma irradiation experiments were carried out under ambient temperature and the irradiation system are described in the Fig 1.

All chemicals used in our experiments were analytical reagent grade. The pH of the I_2 and I_2 solutions were controlled by the addition of 0.1 M NaOH or 0.1 M $HClO_4$ solutions. We used a Metrohm model 654 pH meter, which was calibrated by buffer solutions of pH 4.0 and 7.0 before the pH measurements. The concentrations of I_3^- and I_2 in the irradiated solutions were measured by an ultraviolet-visible (UV-VIS) spectrophotometer (Biochrom model WPA Lightwave II) [1]. We measured the concentrations of CH_3I dissolved in toluene using a GC-MS (Perkin Elmer Clarus 680/SQ 8T, USA). The detection limit of the CH_3I by GC–MS was determined to be 0.048 μM, and the extraction yield of CH_3I was approximately 85% [5].

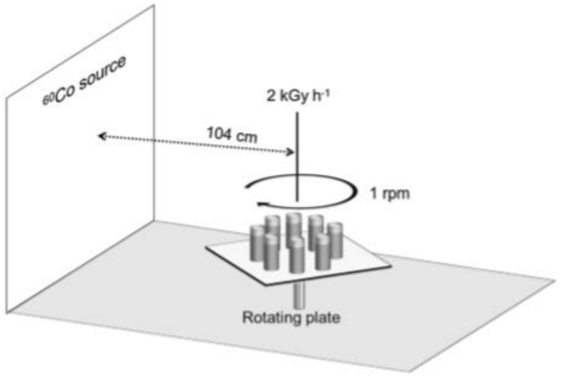

Fig. 1. Schematic diagram of gamma radiation system for iodine experiments [3]

2.2 Gamma Oxidation of Iodide Ion

From the gamma oxidation experiments [2,3], we summarized the main results. We divided the full pH range into three different regions as shown in Fig. 2 [3]. In the first and second regions, I_3^- is basically induced by water radiolysis products such as HO radical and H_2O_2, and by air radiolysis products such as NO_2 (or HNO_3). In the first region, however, the highest level of I_3^- was observed below pH 2 in both aerated and deoxygenated I^- solutions. The additional oxidation reaction in the first region below pH 2.0 is mainly caused by O_2 that is generated from the radiolysis of water. The basis of this interpretation is that I^- was used for the analysis of O_2 concentration in the old analysis history, because I^- is oxidized equivalently by dissolved O_2 into I_3^- in strong acidic (below pH 2.0) solutions. Based on the result, we could obtain information on the O_2 generated from water radiolysis during the irradiation experiments of I^- solutions.

In the third pH region, little I_3^- (or I_2) was formed regardless of the gas purging conditions. In our previous study [2], this phenomenon was demonstrated by H_2O_2 acting as a reductant in this pH range. Thus, at pH above 6, H_2O_2 reduced I_3^- to I^-. In addition, above pH 9, the effect of the disproportionation reaction of I_3^- and I_2 on the behavior of iodine species should also be considered. The contributions of oxidizing and reducing species to iodine behavior at different values of pHs are summarized in Fig. 2.

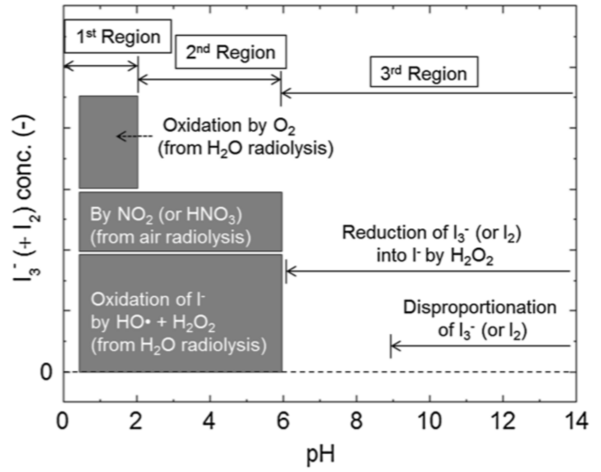

Fig. 2. Contribution diagram of oxidants for I^- oxidation according to pH [3]

2.3 Formation of CH3I

From the formation studies [5] of CH_3I, we drew a diagram (Fig. 3) to describe the whole process of CH_3I formation taking place under our gamma irradiation conditions. In the first stage, the solution pH decreases by decomposition of MIBK and air radiolysis. In the second stage, from which the pH decreases below 6 by the radiolytic decomposition of MIBK. At pH below 6, the I^- starts to be oxidized into I_2. From the experimental data, it was evaluated that the gamma oxidation of I^- into I_2 preferentially occurs rather than the decomposition of the ketone compounds in the mixed solution. In third stage, CH_3I is formed from the reaction of I_2 and $COCH_3$ radical, which also comes from the decomposition of MIBK.

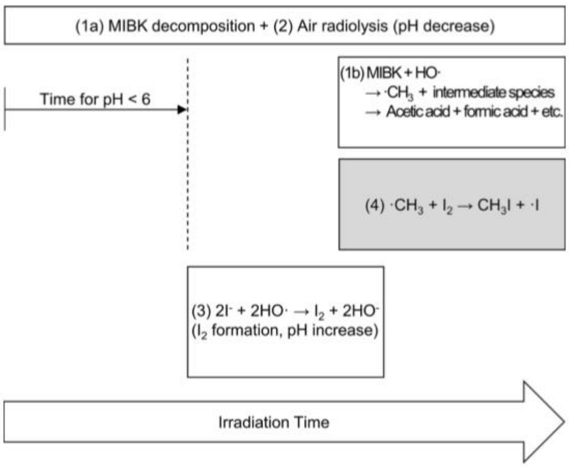

Fig. 3. Diagram of the CH_3I formation processes in NaI and MIBK mixed solutions under gamma irradiation [5]

3. Conclusions

The gamma oxidation of iodide ion to volatile iodine (I_2) was well understood in the pH range between 1 and 12. The oxidizing species in the radiolysis products of water were evaluated according to pH regions. And the role of H_2O_2 in the reduction of I_2 and the disproportionation of I_2 by NaOH were understood by experimental data. The formation of CH_3I under gamma irradiation was also evaluated by the reaction steps depending on the pH. Our results will be helpful to understand the volatility of iodine species under gamma irradiation conditions.

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