Competitive Reaction of OH Radical on Oxidation of Iodide Ion and Decomposition of Methyl Alkyl Ketones

Jei-Won Yeon [a*], Minsik Kim [a,b]
[a]*Nuclear Chemistry Technology Division, Korea Atomic Energy Research Institute, 111, Daedeok-daero 989beon-gil, Yuseong-gu, Daejeon, 34057, Republic of Korea*
[b]*Inhalation Toxicology Research Group, Korea Institute of Toxicology, Republic of Korea*
[*]*Corresponding author: yeonysy@kaeri.re.kr*

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1. Introduction

Under gamma irradiation in the presence of moisture, hydroxyl radicals (OH•), generated from water radiolysis, play a crucial role in determining the fate of iodine species and organic compounds. Specifically, OH• can oxidize iodide (I^-) to molecular iodine (I_2) while also decomposing alkyl ketones, which may contribute to the formation of volatile organic iodine species such as methyl iodide (CH_3I) [1-2]. To examine the competitive interactions between these processes, mixed solutions containing NaI and methyl alkyl ketones (CH_3COR, R = alkyl group) were irradiated with gamma rays, and the concentrations of I_2 and CH_3I were measured. Three ketones (2-butanone, 2-pentanone, and 2-heptanone) were investigated to assess the influence of alkyl chain length on these reactions.

2. Methods and Results

2.1 Experimental Method

Three kinds of mixed solutions containing NaI and methyl alkyl ketone (MAK) were prepared. The methyl alkyl ketones were 2-butanone (MEK), 2-pentanone (MPK), and 2-heptanone (MPNK). These mixed solutions were irradiated at 0-40 kGy under the condition of gamma dose rate of 10 kGy h^{-1}. After irradiation, toluene was added to the irradiated solutions, and I_2 and CH_3I were extracted into toluene phase. The concentrations of I_2 dissolved in toluene were measured by UV-VIS spectrophotometer and CH_3I by GC-MS (Gas chromatograph - mass spectrometer), respectively. The concentration of I^- remaining in the aqueous phase of the irradiated solutions was measured by UV-VIS spectrophotometer. In addition, the pH of the aqueous phase was measured by pH meter. The details of the measurement of I_2 and CH_3I concentrations are described in our previous papers [3-4].

2.2 I_2 Formation in Irradiated Solutions

The effect of pH on I_2 formation in the mixed solution was investigated. The pH was investigated for pH 3 and pH 7. Since I_2 is reduced to I^- by H_2O_2, a radiolytic product of water, at pH 7 or higher, the experiment was not performed under alkaline conditions. In the mixed solution at pH 3, the smaller the chain number of the alkyl group, the higher the concentration of I_2 formed after irradiation. The I_2 concentration did not increase significantly when the irradiation dose was 10 kGy or higher. Even at pH 7, the smaller the chain number of the alkyl group, the higher the concentration of I_2 formed after gamma irradiation. However, the concentration of I_2 formed at pH 7 was overall lower than that formed at pH 3, and the phenomenon of I_2 concentration increasing as the gamma dose increased was observed.

The I_2 concentration measured in the MEK mixed solution is shown in Figure 1. Considering that the NaI concentration is 2 mM, it can be thought that I_2 was formed at a considerably high concentration. When the initial pH is 3, I_2 reaches its maximum formation value at a dose of 10 kGy, and when the pH is 7, I_2 formation continues as the irradiation dose increases to 40 kGy. It is thought that a more accurate analysis will be possible if pH measurement data is added.

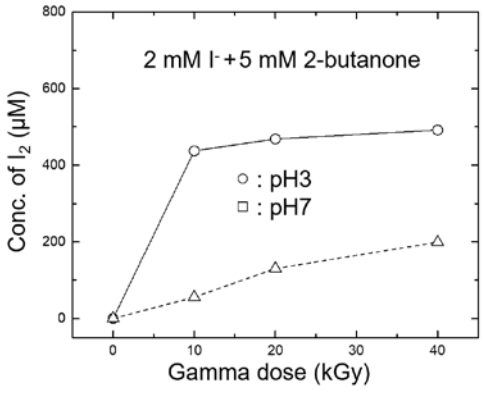

Fig. 1. Concentration of I_2 formed in 2 mM NaI + 5 mM 2-butanone solution (MEK) as a function of gamma irradiation dose (□ :pH 3, □ : pH 7)

2.3 CH_3I Formation in Irradiated Solutions

The effect of the chain number of alkyl group on CH_3I

formation in irradiated solutions was not evident up to 20 kGy at pH 3 conditions, but at 40 kGy, the smaller the chain, the higher the CH_3I concentration was observed. At pH 7 conditions, the effect of the chain number of alkyl ketones was evident from 20 kGy. The concentration of CH_3I was measured in the range of 1-6 uM under 40 kGy irradiation conditions.

The CH_3I concentration measured in the MEK mixed solution is shown in Figure 2. As the gamma dose increased up to 40 kGy at both pH conditions, the CH_3I concentration gradually increased, and overall, the CH_3I concentration was observed to be slightly higher at pH 7. Considering the result that I_2 formation is dominant at pH 3, it can be inferred that there is a competitive step for OH radical in the formation of I_2 and CH_3I.

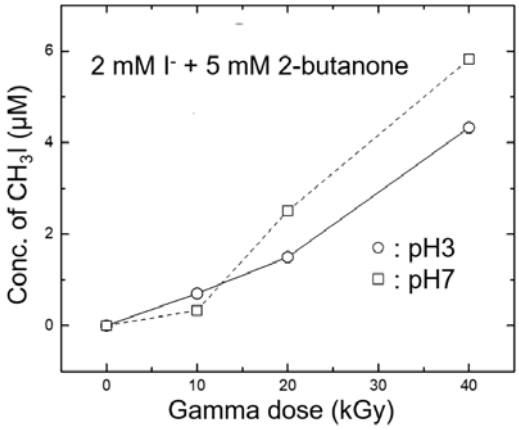

Fig. 2. Concentration of CH_3I formed in 2 mM NaI + 5 mM 2-butanone solution (MEK) as a function of gamma irradiation dose (○:pH 3, □: pH 7)

3. Conclusions

Our results indicate that smaller alkyl groups favor the oxidation of I^- by OH• ($OH• + I^- \rightarrow ½\ I_2 + OH^-$), whereas larger alkyl groups stabilize carbonyl radicals, enhancing their reactivity with OH•. The formation of CH_3I was observed under acidic and neutral conditions but was suppressed in alkaline environments, likely due to the instability of I_2 at high pH. Overall, CH_3I formation was governed by the competition between OH• induced I^- oxidation and ketone decomposition, occurring only when sufficient I_2 was available under pH conditions below 7.

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