

X-ray decomposition of hypervalent iodine compounds induced by iodine *K*-shell excitation

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1 Introduction

Caged compounds are biologically active molecules, such as drugs, rendered inert by attaching photo-removal protecting groups [1]. They allow us to control their biological activities temporally and spatially by photo irradiation. While ultraviolet to infrared light is conventionally used to activate the caged compounds [2], we propose the use of X-rays in an attempt to increase the penetration depth of the activation light in living bodies.

In this work, we report an X-ray induced decomposition reaction of a hypervalent iodine compound, 4-carboxy-2-iodosobenzoic acid (IBA-COOH; Fig. 1(a)), which is one of the promising protecting groups for the X-ray activated caged compounds.

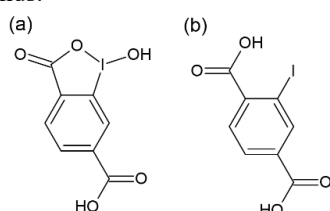


Fig. 1: Structures of (a) IBA-COOH and (b) ITPA.

2 Experiment

The powder of IBA-COOH was dissolved in 1 mM phosphate buffer (pH6.8). The concentration of IBA-COOH was *ca.* 0.5 mM. The solution was irradiated with the 33.10 and 33.45 keV X-rays, corresponding to the pre- and above-edge regions of iodine *K*-edge, respectively. Each dose rate was *ca.* 30 Gy/h. One hundred microliter solution was collected every 4 h of irradiation. The collected solution was analyzed using an LC-MS system.

3 Results and Discussion

For all irradiated samples, 2-iodoterephthalic acid (ITPA; Fig. 1(b)) was detected as a decomposition product by the LC-MS analysis (data not shown). Figures 2(a) and 2(b) show the dose dependence of IBA-COOH decomposition and ITPA production, respectively. The decomposition yield for the 33.10 keV irradiation was lower than that for the 33.45 keV irradiation (Fig. 2(a)). It is reasonable because the irradiation energy of 33.10 keV was below the iodine *K*-edge, resulting in fewer decomposition reactions. On the other hand, the production yield for the 33.10 keV irradiation was higher than the other (Fig. 2(b)). The secondary electrons produced by the 33.45 keV irradiations would induce the non-specific bond breakages more than those produced by the 33.10 keV

irradiations and therefore the production of ITPA was relatively inferior. Resonant iodine *K*-shell excitations also exhibited similar results (see details in our paper).

Thus, the I-O bond scissions were induced by X-ray irradiation to the IBA-COOH solution.

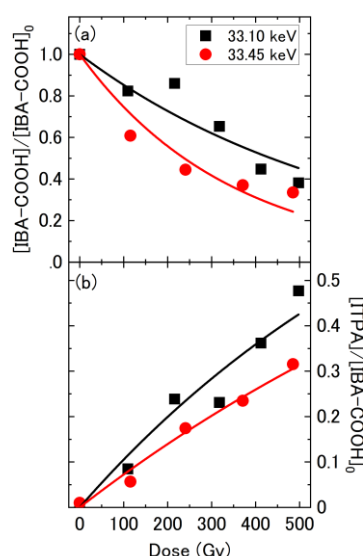


Fig. 2: The dose dependence of (a) IBA-COOH decomposition and (b) ITPA production. The $[X]_0$ and $[X]$ indicate the concentration of *X* before and after irradiation (*X*=IBACOOH, ITPA).

4 Conclusions

The decomposition of IBA-COOH was induced by the ~33 keV X-ray irradiations. The I-O bond scission would be a promising reaction to design the X-ray activated caged compounds.

Acknowledgement

This work was supported by JST, CREST, Japan [Grant Number JPMJCR 1902].

References

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Research Achievement

Y. Izumi *et al.*, *Rad. Phys. Chem.* **237**, 112992 (2025).

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