

Preliminary Report on Bonding State of Carbon in Organochlorine Compounds by Using Peak Position of C *K*-edge NEXAFS

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1 Introduction

Organochlorine compounds are known as hazardous organics which derived from natural processes and anthropogenic activities. Polychlorinated dibenzo-*p*-dioxins, dibenzo furans, biphenyls, and chlorobenzenes are unintentionally generated by various thermal and anthropogenic processes. Some of them are involved in persistent organic pollutants (POPs).

Formation mechanisms of these toxic organochlorine compounds were revealed by X-ray absorption techniques. Recent our studies reported catalyst-like mechanism of metals during thermochemical formation of organochlorine compounds [1-4]. Although these studies selected X-ray absorption fine structure of transition metal as analytical technique, thermochemical interaction between various elements and carbon matrix was still unknown.

Near-edge X-ray absorption fine structure (NEXAFS) of carbon *K*-edge was measured by soil scientists and geoscientists to understand chemical state of carbon in natural soils and rocks. And, there are some database of C *K*-edge NEXAFS [5,6]. However, bonding state of carbon in organochlorine compounds was not measured systematically in such research fields. In this study, we reported preliminary dataset of C *K*-edge NEXAFS of organochlorine compounds.

2 Experiment

We measured C *K*-edge NEXAFS at BL-11A in KEK-PF (Tsukuba). 36 organic compounds were selected. These compounds had various bonding states of carbon (C-C, R-OH, R-COOH, R-O-R', C-Cl, and C-N). To avoid contamination of carbon, we put sample powders on indium plate. The indium plate with sample was fixed on sample bar. After sample chamber was kept high vacuum, we measured C *K*-edge NEXAFS by total electron yield (TEY) method.

3 Results and Discussion

Conventional spectrum of C *K*-edge NEXAFS was shown in graph during 280-310 eV. However, BL-11A did not measure this range well, because photo-current intensity decreases at C *K*-edge by using holographic diffracting grating (300 l/mm). In this our first trial, we found that spectrum of C *K*-edge NEXAFS was correctly measured during 283-290 eV at BL-11A. So, maximum peak position of C *K*-edge NEXAFS could be used for characterization of bonding state of carbon.

Fig.1 shows Maximum peak positions (MPs) of C *K*-edge NEXAFS in various organic compounds ($n = 36$). Aromatic compounds without any functional groups ($n = 8$) showed MPs at 284.85 ± 0.68 eV. In case of existence

of oxygen atom in aromatic compounds ($n = 10$) such as R-OH, R-COOH, and R-O-R', MPs concentrated at 287.93 ± 0.046 eV. We found that organochlorine compounds had characteristic MPs at 288.34 ± 0.034 eV ($n = 7$). In case of 2,3-Cl coordination of aromatic ring, MPs were at 286.88 ± 0.46 eV ($n = 3$) which lower than that of other organochlorine compounds. In contrast, aromatic compounds with nitrogen atom ($n = 8$) did not have characteristic MPs.

These findings would contribute to analysis of thermochemical interaction between various elements and carbon matrix during formation and inhibition of organochlorine compounds in solid phase.

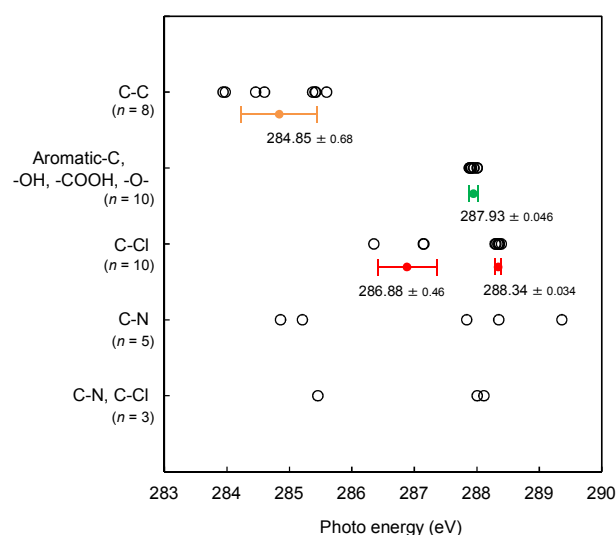


Fig. 1: Maximum peak positions of C *K*-edge NEXAFS in various organic compounds ($n = 36$).

References

- [1] T Fujimori and M Takaoka, *Env. Sci. Tech.* **43** (2009) 2241.
- [2] T Fujimori *et al.*, *Env. Sci. Tech.* **44** (2010) 1974.
- [3] T Fujimori *et al.*, *Env. Sci. Tech.* **45** (2011) 7678.
- [4] T Fujimori *et al.*, *Env. Sci. Tech.* **47** (2013) 2169.
- [5] O Dhez *et al.*, *J. Electron. Spectrosc. Relat. Phenom.* **128** (2003) 85.
- [6] Gas Phase Core Excitation Database, McMaster Univ., <http://unicorn.mcmaster.ca/corex/cedb-title.html>

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