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Acceleration of halogen-exchange reaction of lead(II) fluoride in organic solvent

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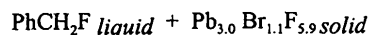
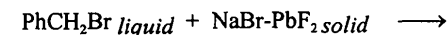
A combination of lead (II) fluoride and a small amount of sodium bromide accelerates the halogen-exchange reaction of benzyl bromide to benzyl fluoride in acetonitrile. By analyzing Br *K*-EXAFS for both the combined reagent and aliquots taken from the reaction mixture, bromide-participating species has been found in both the combined reagent and the initial stage of the reaction. Such species disappeared with proceeding of the reaction and a new lead compound, $\text{Pb}_{3.0}\text{Br}_{1.1}\text{F}_{5.9}$ (**1**) was formed. The evidence suggests that the bromide-participating species initially formed in the combined process between lead fluoride and sodium bromide act the high reactivity for the organic fluorination.

Keywords: Br *K*-EXAFS; lead fluoride; combined solid reagent; organic fluorination

1. Introduction

The use of inorganic solid surface in organic reactions is a rapidly growing area of interests owing to its possibility of the control of reactivity and/or selectivity. We have studied the use of synergistic interactions between diverse inorganic solid reagents for enhancing solid-liquid heterogeneous reactions with organic compounds dissolved in organic solvents. A combination of lead fluoride (II) and a small amount of sodium bromide has been recently found to be an efficient solid reagent for accelerating the fluorinations of organic halides and the Friedel-Crafts-type alkylations with alkyl halides [Ichihara, 1992,1995,1997]. These reactions are basic and important for preparing the intermediates of fine organic chemicals and our solid reagent provides one of the convenient synthetic methods.

Based on organic and inorganic analyses the whole heterogeneous fluorination scheme using the combined reagent is described as below.



With acceleration of the organic reaction, the combined reagent is converted to a new inorganic lead compound, $\text{Pb}_{3.0}\text{Br}_{1.1}\text{F}_{5.9}$ (**1**)*, whereas lead fluoride alone is converted to PbBrF . As the

compound **1** has not high activities for the organic fluorination as well as PbF_2 , another species for inducing the organic reaction should exist in the combined process of NaBr and PbF_2 . Not only reaction species but also reaction process remains ambiguous, because the active species arising from a small amount of sodium bromide seems to be small and such species could not have the long range ordering. Thus the XAFS investigation has been carried out to elucidate the active species for the present combined NaBr- PbF_2 reagent.

2. Experimental Section

The combined process between lead fluoride powder and sodium bromide powder (1.00/0.04 molar ratio) with or without acetonitrile solvent and the subsequent organic reaction process were followed by XAFS. The heterogeneous reaction of benzyl bromide and the combined NaBr- PbF_2 was carried out in acetonitrile at 90 °C. The series of the liquid-solid heterogeneous aliquots taken from this reaction mixtures periodically was prepared for XAFS measurements. XAFS spectra of *K*-absorption edge of Br and *L*III-absorption edge of Pb were measured at BL-6B in the Photon Factory of the National Laboratory for High Energy Physics in Tsukuba, with 2.5 Ge V positrons. The incident X-ray was monochromatized with Si(111) double crystals. For comparison, XAFS measurements were carried out in the reaction of lead fluoride and benzyl bromide in acetonitrile.

3. Results and Discussion

XAFS spectra of Br *K*- and Pb *L*III-absorption edges were obtained for the inorganic lead compound **1** and PbBrF . The compound **1** is formed from lead fluoride (PbF_2) and sodium bromide (NaBr) in acetonitrile solvent without the organic reaction. XAFS spectra of *K*-absorption edge of Br were measured through this process.

As shown in Fig. 1, a new peak near 0.23 nm appeared on the Fourier transform of the Br *K*-EXAFS (c) after mixing a small amount of NaBr powder with PbF_2 powder in acetonitrile at room temperature. The new peak decreased as the formation of **1** increased. By raising the reaction temperature to 90 °C the peak was diminished and the mixture was completely converted to the compound **1** (d). Interestingly, the peak was more clearly observed when NaBr and PbF_2 powder were mixed without solvent at room temperature (b). The peak was not observed for the related bromide compounds such as NaBr (a), **1** (d), PbBrF , and PbBr_2 . These results suggest the formation of a new species by interaction between two solids under these conditions.

For the organic reaction process of benzyl bromide and the NaBr- PbF_2 in acetonitrile Br *K*-EXAFS spectra showed substantial local difference around Br in comparison with Pb *L*-EXAFS: The peak near 0.23 nm appeared immediately after starting the organic reaction and during the reaction. In the case of the reaction of lead fluoride and benzyl bromide in acetonitrile, the Br *K*-EXAFS did not involve the peak. Thus, the corresponding species to the peak may contribute to the reaction process.

By these XAFS analyses, we have first found that a bromide-participating species is initially formed in the combined process of PbF_2 and a small amount of NaBr. The species can operate as an active species for inducing the heterogeneous reaction of benzyl bromide and the NaBr- PbF_2 into benzyl fluoride and **1**, although it is still not elucidated how sodium cation and bromide anion of NaBr participate with solid surface of lead fluoride to form the species and what its structure is. In conclusion, a new species which could contribute to accelerating the halogen-

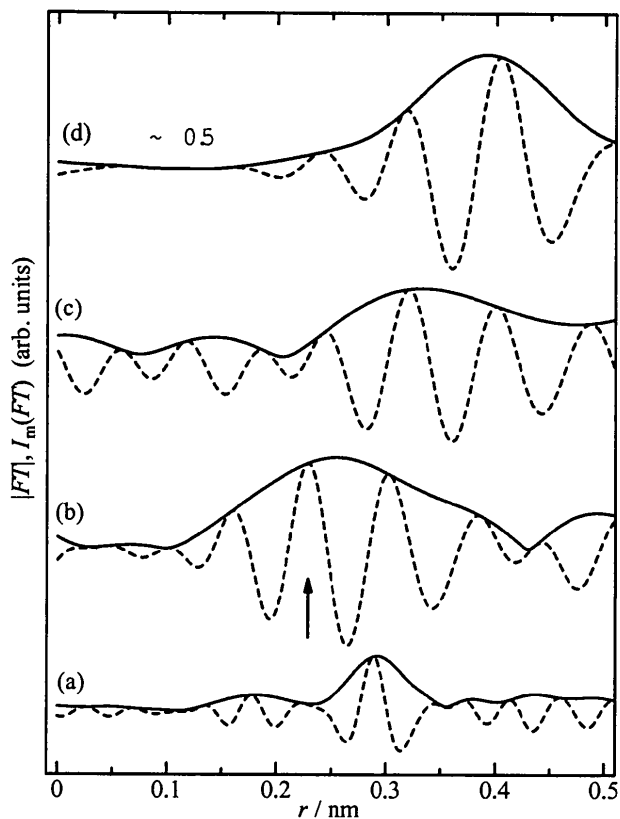


Figure 1

Variation of Fourier transforms for the Br *K*-EXAFS in the conversion of NaBr and PbF₂ into the compound 1. (a) NaBr, (b) the mixture of NaBr and PbF₂, (c) NaBr and PbF₂ in acetonitrile at rt, and (d) NaBr and PbF₂ in acetonitrile with heating (the compound 1). Fourier transforms of k^3 weighted EXAFS function in the range of $k = 2.7 - 12.8 \text{ \AA}^{-1}$ (a), $1.4 - 6.7 \text{ \AA}^{-1}$ (b), $2.5 - 5.2 \text{ \AA}^{-1}$ (c), and $1.2 - 5.8 \text{ \AA}^{-1}$ (d).

exchange reaction using the combined lead fluoride was first captured by XAFS analyses. This finding has been not performed by other analyzing means such as X-ray diffractometry because of a partial reaction of a small amount of NaBr.

Acknowledgements

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*The obtained compound I was found to be composed of Pb_{3.0}Br_{1.1}F_{5.9} by X-ray fluorescence analysis.

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