

XPS Investigation of A³ Coupling Reaction in Room Temperature Ionic Liquids

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We herein report a new analytical application of XPS to the identification of organic molecules in room temperature ionic liquid for the first time. An organic compound, propargylamine (**1**), produced in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), which is one of the room temperature ionic liquids (RTILs), via A³ coupling reaction, is characterized by means of x-ray photoelectron spectroscopy (XPS) rather than using conventional organic compound analysis techniques. There are four non-equivalent carbons in RTILs and **1** each. The ratios of normalized integrated areas of the deconvoluted binding energy of core electron of carbon (C1s) peaks are well matched to the number of carbons in those compounds. The binding energies of C1s of the featured carbons in **1**, C4 (sp carbons in acetylene group) and C5 (sp² carbons in benzene ring), are assigned 286.2 and 285.4 eV, respectively. These results will be able to provide an important tool and a new strategy for the analysis of organic molecules

Key Words : X-ray photoelectron Spectroscopy, Ultra-high vacuum, A³ coupling reaction, Room temperature ionic liquid

Introduction

X-ray photoelectron spectroscopy (XPS) has been limited to characterize solid samples for identification of elemental composition and verification of chemical environments of atoms so far because of the requirement of their low vapor pressure.^{1,2} The XPS analysis has performed in ultra high vacuum (UHV) condition in order to reduce the interference from gas phase scattering since the signal from the surface is very weak. To perform XPS experiment, samples must have low vapor pressures, stability even in UHV condition and sufficient photoelectron yield as solid samples.

Recently a variety of organic reactions, transition metal-catalyzed reactions, and biotransformations have been extensively studied in RTILs³⁻⁶ and many analytical applications were applied to characterize RTILs systems.⁷⁻¹² RTILs are very fascinating reaction media against conventional organic solvents due to their unique properties such as non-detectable vapor pressure, environmental safety, reusability, reasonable thermal stability, polarity, and good solubility for organic, inorganic, and organometallic compounds.¹³⁻¹⁵ These characteristics of RTILs perfectly satisfy the criteria for using XPS to monitor catalytic organic reactions in RTILs.

We synthesized propargylamine (**1**) through A³ coupling reaction (alkyne (phenylacetylene), aldehyde (benzaldehyde) and amine (piperidine)) in 1-*n*-butyl-3-methyl-imidazolium hexafluorophosphate, [bmim][PF₆],¹⁶ then we monitored the reaction using XPS in UHV condition without any treatments. We report here a new field for identification of organic compounds in RTILs using XPS.

Experimental Section

A³ coupling (three-component coupling of aldehydes, alkynes and amines) was carried out as follows. A mixture

of [bmim][PF₆] (1 mL) and CuI (1.9 mg, 0.01 mmol, 2 mol% as a catalyst) was degassed under reduced pressure at 80 °C for 30 min, and then N₂ was introduced. To the solution were added piperidine (75 μL, 0.75 mmol), benzaldehyde (51 μg, 0.5 mmol) and phenylacetylene (67 μL, 0.6 mmol), and the resulting mixture was heated at 120 °C for 2 h with stirring. The reaction mixture was cooled and extracted with diethyl ether (5 mL × 5). The combined organic layer was concentrated and the crude mixture was purified by flash chromatography on silica gel with eluent of *n*-hexanes-ethyl acetate (10 : 1). For tracking the reaction profile, 100 μL aliquots were taken from the reaction vessels every 15 minutes.

Monitoring of the reaction was carried out in an ultra high vacuum (UHV) chamber (base pressure 5 × 10⁻¹⁰ mbar) equipped with a concentric hemispherical analyzer (CHA) and a twin anode X-ray source (Mg/Al Kα 1253.6 and 1486.6 eV, respectively) for XPS (VG ESCALAB 2000). The XPS chamber was pumped by two stages of pumping system. The first one is that a turbomolecular pump (TMP) backed by a two stage rotary vane pump (RP) system pumps a fast entry air load-lock (FEAL) chamber. And the second system consists of an ion getter pump and a Ti-sublimation pump and evacuates analysis chamber to maintain UHV condition. An ion sputtering gun is equipped in the analysis chamber for sample cleaning and depth profile study. A charge-coupled device (CCD) camera guides to set up the sample for x-ray photoelectron analysis.

During survey scans, spectra were obtained using Mg Kα x-ray source. X-ray source was at high voltage of 15 kV, beam current of 15 mA, filament current of 4.2 A, pass energy of 50 eV, dwell time of 50 ms and energy step size of 1 eV in constant analyzer energy (CAE) mode at large area XPS (LAXPS). High resolution spectra were obtained at pass energy of 20 eV, energy step size of 0.05 eV and other factors were kept the same as survey scan. Under these

conditions, aliphatic carbon 1s peak was corrected to 285 eV.^{17,18} Each aliquot taken every 15 minutes from the start of the experiment is pre-pumped in the FEAL chamber for 2 hrs before loading into the analysis chamber which was pumped by a TMP (70 l/s) backed by an RP (200 l/min). Our XPS data were deconvoluted using XPSPEAK software (ver 4.1). Obtained XPS C1s peaks were divided into several peaks according to their chemical environments. The FWHM of each peak was between 1.2 and 1.9 eV, and G/L ratio of 30% (Lorentzian-30%, Gaussian-70%).

Results and Discussion

Figure 1 shows high resolution C1s XP spectra of pure [bmim][PF₆] and the product **1** of A³ coupling reaction in RTILs by reaction time from the bottom. Even the RTILs are pure, the C1s XP spectra look like combining several peaks because there are four nonequivalent carbons in [bmim]-[PF₆]. The C1s peak around 285 eV is evolved by the reaction time. This peak is caused by the carbons in benzene ring, which are the featured carbons of **1**. The details of the components of pure RTILs and **1** in solution of RTILs are shown in Figure 2 and 3, respectively. In order to check whether the featured C1s photoelectron signal comes from product or not, we made three RTILs solutions which contained same amount of reactants (piperidine, phenylacetylene, benzaldehyde) each and pumped in the FEAL chamber for 2 h as the reacted aliquots prepumped. Bubbles were observed during prepumping process from the RTILs

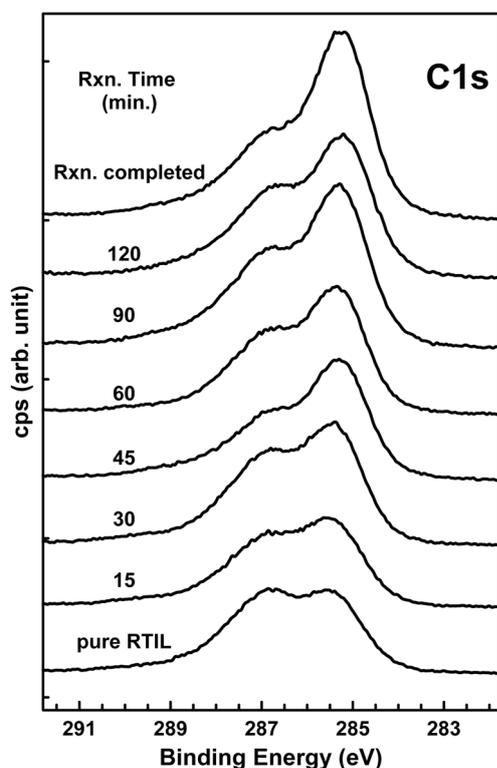


Figure 1. High resolution XP spectra of C1s photoemission of propargylamine (**1**) in [bmim][PF₆] by A³ coupling (three-component coupling of aldehydes, alkynes, and amines) reaction time.

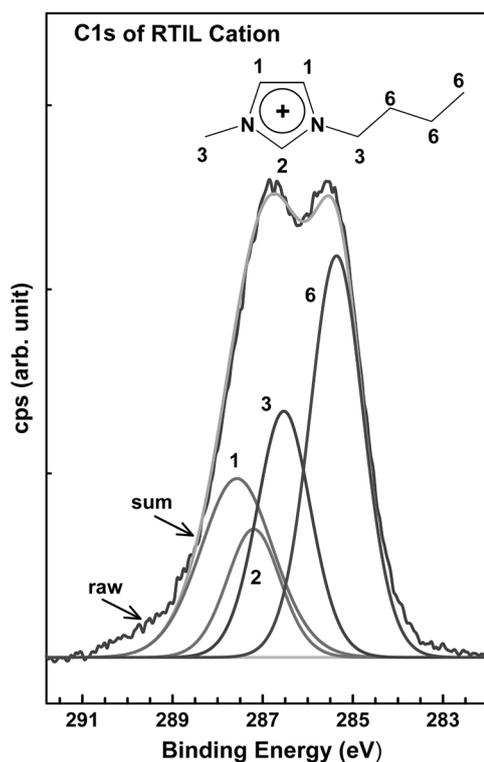


Figure 2. Detailed C1s photoemission of pure 1-*n*-butyl-3-methylimidazolium cation. Top two peaks are sum of deconvoluted C1s (smooth line) and raw data (wiggled line). The inset shows the chemical structure of 1-*n*-butyl-3-methylimidazolium cation.

solution with reactants. We could not detect the C1s photoelectron signal coming from the reactants (not shown here). This means that the unreacted reactants, which have relatively low boiling points, were evaporated completely in the FEAL chamber before the aliquots were installed in the analysis chamber. Therefore it can be ruled out that some featured C1s photoelectron signal in Figure 3 came from the unreacted reactants. XPS analysis is sensitive enough to give us the chemical information of organic carbons in RTILs.

Figure 2 and 3 show the detailed C1s XP spectra of pure RTILs and **1** in RTILs respectively. The normalized relative areas of nonequivalent C1s peaks were fixed by the stoichiometries of the [bmim][PF₆] and **1**. We assigned the binding energies of C1s photoelectron of each deconvoluted peak based on the chemical environment of the carbons.¹⁸ We labeled the carbons according to the binding energy of C1s photoelectron from high to low. The aliphatic carbons (C6) are corrected to 285.0 eV.¹⁷ The binding energy of C1 (287.9 eV) is assigned higher than that of C2 (287.4 eV) because the C2 hydrogen participates in hydrogen-bonding with hexafluorophosphate anion.¹⁹ In Figure 3, we can see new featured peaks (C4 and C5; 286.2 and 285.4 eV respectively) of **1** and larger peaks (C3 and C6; 286.7 and 285.0 eV) compared with C1s peaks of pure [bmim][PF₆] (Figure 2).

Figure 4 shows the ratio of normalized integrated areas of detailed C1s peaks in different chemical environment by the reaction time. There is only pure [bmim][PF₆] before the A³ coupling reaction occurred (reaction time = 0). The ratio of

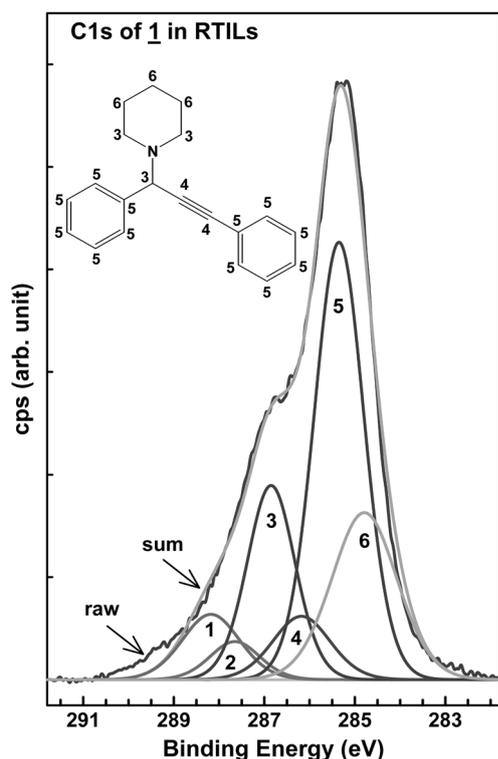


Figure 3. Deconvoluted peaks of C1s photoelectron emission of propargylamine, **1**, in RTILs. The peaks labeled as C1 and C2 carbons are originated from RTIL and top two peaks are sum of deconvoluted C1s (smooth line) and raw spectra (wiggled line). The inset shows the molecular structure of the product, propargylamine, of the A^3 coupling reaction.

integrated areas of carbons labeled 1 : 2 : 3 : 6 is 1.9 : 1.0 : 1.9 : 3.1. We assumed the photoelectron sensitivities of the carbons in organic compounds are same when we calculate the peak area ratio. This ratio from experimental results is well matched with the number of carbons in [bmim][PF₆], 2 : 1 : 2 : 3, within experimental error. As the A^3 coupling reaction progressed, the integrated areas of featured peaks of **1** (C4 and C5) and peaks of C3 and C6 increased gradually. The integrated areas of C3 and C6 are contributed from [bmim][PF₆] and **1**. After we subtracted the contribution of [bmim][PF₆] from the peak areas of XP spectra obtained from completed reaction, the ratio of integrated areas of carbons labeled 3 : 4 : 5 : 6 is 3.1 : 2.0 : 12.3 : 2.9 in the product in RTILs solution. This ratio is close to the number of carbons in **1**, 3 : 2 : 12 : 3. This is the first result to characterize an organic compound in RTILs under UHV condition.

Conclusions

In this research, an organic compound **1**, which was obtained by A^3 coupling using [bmim][PF₆] as a solvent, was characterized in RTILs solution by XPS analysis without any purification processes. This analytical application is a new field to identify organic compounds with relatively high boiling points in RTILs. The ratio of integrated areas of

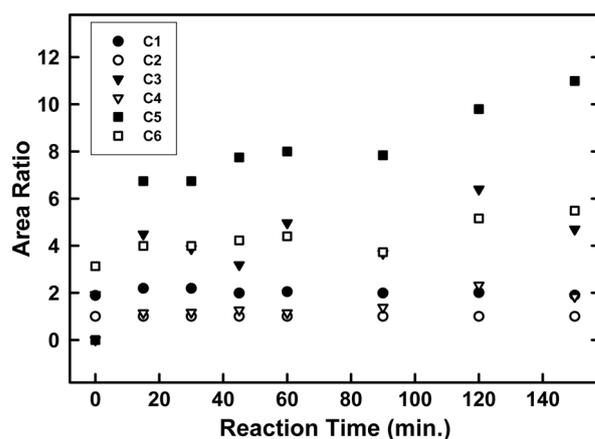


Figure 4. Integrated areas of C1s photoelectron in different chemical environments determined from the spectra such as those in Figure 2 and 3.

deconvoluted C1s peaks is well matched to the number of non-equivalent carbons in propargylamine as well as RTILs within experimental error. We anticipate that these results will provide an important tool and a new strategy for the analysis of organic molecules.

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