VIP **Ionic Liquids**

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Monitoring of Liquid-Phase Organic Reactions by Photoelectron Spectroscopy**

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In recent years, surface-science studies of ionic liquids (ILs) have attracted increasing scientific interest.[1–3] The properties of ILs make them attractive for applications in catalysis,[4–6] separation processes,[7] and electrochemistry.[8] ILs are defined as salts with a melting point below 100 °C, and they are characterized by extremely low vapor pressures.[9,10] The low volatility allows to address fundamental and mechanistic questions by ultrahigh vacuum (UHV) methods that were originally developed for solids. X-ray photoelectron spectroscopy (XPS), also denoted as electron spectroscopy for chemical analysis (ESCA), has been proven to be one of the most powerful methods to quantitatively analyze the chemical composition of the near-surface region of ILs.[2] Since core-level binding energies are sensitive to the local chemical environment, XPS also allows the determination of the chemical state (e.g., oxidation state) of particular atoms in the near-surface region of an IL.

In contrast to classical spectroscopy tools in chemistry, the advantage of reaction monitoring with XPS (denoted "in situ XPS") is the ability to monitor all elements (apart from hydrogen and helium) simultaneously with respect to their quantity and their chemical state under well-defined (ultraclean) conditions. Moreover, XPS focuses only on the near-surface region, which is not possible with most other methods. The inherent surface sensitivity of XPS originates from the small inelastic mean-free path of photoelectrons in matter[11] which for ILs results in a typical information depth below 9 nm under an electron-emission angle of 0° (with respect to the surface normal).[12] By changing the emission angle to 80° (angle-resolved XPS, ARXPS) the information depth can be further lowered to approximately 1.5 nm. An increase of a particular core level with an increasing detection angle, and thus with increasing surface sensitivity, indicates a higher concentration of the element in the topmost layers as compared to the "bulk", thus enabling conclusions on orientation and/or enrichment of molecules at the surface.

The growing number of surface science studies of ILs under UHV conditions has not only increased our specific knowledge on molten salt surfaces but also opened new routes toward the fundamental understanding of the surface properties of liquids in general.

Herein, we now demonstrate that in situ XPS offers a new and general approach for the monitoring and mechanistic understanding of ordinary liquid phase organic reactions, if the reacting groups have been linked before-hand to an ionic head group to drastically lower the vapor pressures of the reactants. Our contribution demonstrates this approach for the nucleophilic substitution reaction of an alkyl amine and an alkyl chloride moiety, which are attached to the cation and anion of ionic liquids, respectively. This novel approach offers fundamentally new possibilities to gain insight into the reactions of organic liquid-phase systems, including information on surface composition and orientation, involvement of different oxidation states in the proceeding reaction, and kinetic investigations under solvent-free ultraclean UHV conditions.

To date, only a few experiments have been carried out by using in situ XPS for IL systems, that is, to follow reactions or dissolution processes in an XP spectrometer. Lovelock et al. studied the in situ adsorption, dissolution, and desorption of water on $[C_8C_1Im][BF_4]$ by temperature-programmed XPS.[13] Licence and co-workers followed the in situ electrochemical oxidation of metallic Cu to Cu^+ in an IL[14] and the electrochemical reduction of Fe^{3+} to Fe^{2+} in an IL,[15] and Compton et al. measured the electrodeposition of potassium metal from an IL.[16] Kötz et al. also dealt with in situ electrochemical XPS, but concentrated on the effect of the applied potential on the binding energy and stability of $[C_2C_1Im][BF_4]$.[17] Finally, the partial exchange of CO molecules adsorbed on Pd nanoparticles on an Al_2O_3/NiAl(110) substrate by the IL $[C_4C_1Im][Tf_2N]$ was monitored by Sobota et al., who used IR and in situ XP spectroscopy.[18] All of the above-mentioned experiments dealt either with a reaction at an interface or with an electrochemical reaction, and in all cases nonfunctionalized ILs were employed.

For our study of in situ XPS reaction monitoring, we selected the reaction of 1-ethyl-3-methylimidazolium 4-chlorobutylsulfonate $[C_2C_1Im][ClC_4H_8SO_3]$ (IL**1**) and 1-methyl-3-(3′-dimethylaminepropyl)imidazolium trifluoromethylsulfo-

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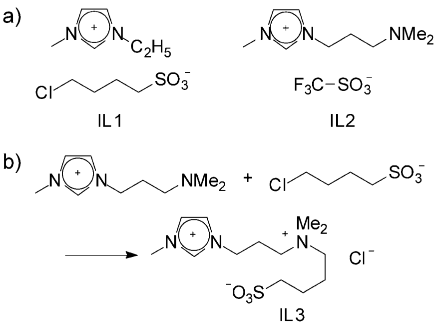
nate [(Me$_2$NC$_3$H$_6$)C$_1$Im][TfO] (IL**2**) as a model system. IL**1** was obtained by reacting [C$_2$C$_1$Im]Cl with 1,4-butane sultone according to a reported procedure,[19] IL**2** was prepared by reacting 3-chloropropyldimethylamino hydrochloride and *N*-methylimidazole in water, followed by anion metathesis (see the Supporting Information for details). In the course of the reaction of IL**1** and IL**2**, the amine functionality of IL**2** is alkylated by the 4-chlorobutylsulfonate anion of IL**1** (Scheme 1) to form the new zwitterionic salt IL**3**, and [C$_2$C$_1$Im][TfO] as the second product.

Prior to our XPS investigations, the reaction was carried out under standard laboratory conditions and routine ^{1}H NMR analysis was applied to analyze the product mixture. After heating a 1:1 mixture of neat IL**1** and IL**2** to 100 °C for 90 minutes and dissolving the final product in [D$_6$]-DMSO, the ^{1}H NMR spectra showed only minor changes. For instance, the methyl groups of NMe$_2$ in IL**2** (singlet signal at 2.2 ppm, presumably most affected by the alkylation) shifted less than 0.1 ppm downfield, thus making an unambiguous quantitative NMR analysis virtually impossible. To verify if the alkylation indeed took place under the applied conditions, an electrospray ionization (ESI) mass spectrum of the product was recorded and clearly showed the presence of an $m/z =$ 304.2 species, which can be unambiguously attributed to the formation of the IL**3** cation.

XPS requires UHV conditions and the exposition to X-ray irradiation. Both these factors in combination with an elevated temperature could affect the stability of primary ionic liquids. Therefore, at first ARXPS measurements of both neat-substrate ILs were conducted at elevated temperatures. For IL**2** no changes in the XP spectra were observed after 2 hours at 100 °C, thus validating the stability of IL**2** under the reaction conditions that were later used for the nucleophilic substitution reaction (see below). Furthermore, the analysis of the angle-resolved XP spectra showed a preferred orientation of the amine-functionalized cation at the IL**2**–vacuum interface: The corresponding N 1s spectra (Figure 1, 0° (black) and 80° (green) emission) clearly show two signals. The signal at 401.9 eV originates from the two imidazolium nitrogen atoms (N$_{\text{imid}}$) and the signal at 399.2 eV from the amine functionality (N$_{\text{amine}}$). When increasing the emission angle from 0° to 80°, the N$_{\text{amine}}$ signal increases and the N$_{\text{imid}}$ signal decreases. This behavior is attributed to a preferential orientation of the cation with its amine functionality pointing toward the vacuum and the imidazolium ring into the bulk.



Scheme 1. a) Structure of IL**1** and IL**2**, and b) Alkylation of the IL**2** cation by the IL**1** anion to form IL**3** (and [C$_2$C$_1$Im][TfO]).

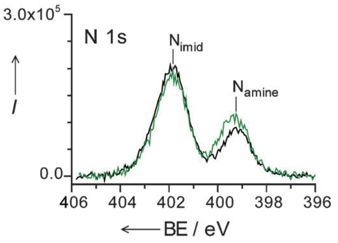


Figure 1. N 1s region of IL**2** at room temperature in 0° (black) and 80° (green) emission; BE = binding energy; *I* = intensity in counts per second.

In contrast to IL**2**, IL**1** showed pronounced signs of decomposition of the 4-chlorobutylsulfonate anion in UHV at 100 °C. The left-hand side of Figure 2 shows the Cl 2p and the O 1s XP spectra at 0° emission, before (black) and after (red) heating IL**1** in situ for 2 hours at 70 °C and 1.5 hours at 100 °C; the corresponding C 1s, N 1s, and S 2p spectra are shown in Figure S1 in the Supporting Information. Before heating, the Cl 2p region shows a doublet structure, due to the spin-orbit split 2p$_{1/2}$ and 2p$_{3/2}$ components. The Cl 2p$_{3/2}$ signal has a binding energy of 200.5 eV, which is representative for covalently bound chlorine (Cl$_{\text{cov}}$).[19] Upon heating to 70 °C, the XP spectra remain nearly unchanged (not shown). However, upon further heating to 100 °C for 1.5 hours, the intensity of the original Cl doublet decreases to about 45 %, and simultaneously a new doublet arises, with the Cl 2p$_{3/2}$ signal at 197.2 eV. The latter is assigned to a chloride species (Cl$_{\text{ion}}$, by comparison to XPS measurements of [C$_8$C$_1$Im]Cl).[20] Furthermore, a concomitant decrease of the intensities of O 1s (Figure 1) and S 2p (Figure S1) is observed. These observations indicate that a reversal of the ring-opening reaction, which was employed to prepare IL**1**, occurs upon heating the IL in vacuum (see Scheme 2 a). In situ mass spectrometry during the heating step shows the characteristic pattern of 1,4-butane sultone (in the gas phase), thus

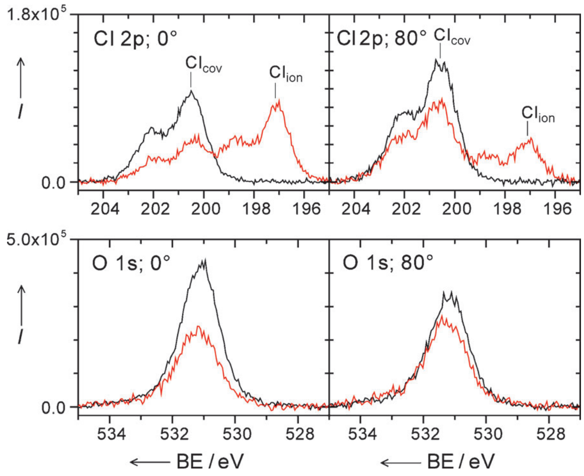
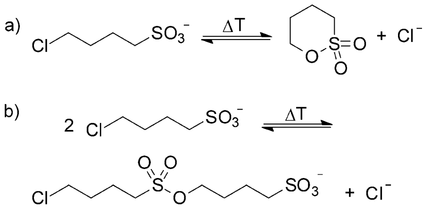


Figure 2. Cl 2p and O 1s XP spectra of IL**1** before (black) and after heating to 70 °C for 2 hours and additional heating to 100 °C for 1.5 hours (red) in 0° emission (left) and 80° emission (right); note the identical intensity scales in 0° and 80° emission.



Scheme 2. a) Sultone formation and b) formation of a 4-chlorobutylsulfonate ester by self-reaction of the 4- chlorobutylsulfonate anion.

confirming the reverse reaction (see Figure S2 in the Supporting Information).[21] A thermal gravimetric analysis (TGA) of similar compounds with the same 4-chlorobutylsulfonate anion and different cations showed a decomposition of the anion to 1,4-butane sultone and the corresponding chloride salt between 210 and 215 °C at standard pressure.[19] However, in our UHV apparatus a much lower temperature is sufficient for this decomposition to occur, since the sultone is steadily removed from the equilibrium under the vacuum conditions.

The comparison of the intensities in the Cl 2p and O 1s regions shows that the intensity of the Cl_{cov} signal decreases to (45 ± 5) % and the intensity of the O 1s signal decreases only to (58 ± 5) %. This is a clear indication that not only sultone formation (which would lead to an identical decrease), but also an additional reaction occurs. A possible explanation is the formation of a sulfonic acid ester by self-reaction of the chlorobutylsulfonate (Scheme 2 b). Because of the anionic nature of the ester that is formed, it does not evaporate and therefore contributes to the O 1s signal.

Information about the orientation and the enrichment of the ions at the surface is again obtained from the 80° emission spectra, which are shown on the right-hand side of Figure 2. Before heating **IL1** (spectra in black), an increase in Cl 2p (Cl_{cov}) and a decrease in O 1s intensity is observed at 80°, as compared to 0°, thus suggesting an orientation of the $[ClC_4H_8SO_3]^-$ anion with its chlorobutyl chain sticking out into the vacuum while the sulfonate group points toward the bulk. After heating at 100 °C (spectra in red in Figure 2), the Cl_{cov} signal at 80° is larger than at 0°, whereas the Cl_{ion} signal shows the opposite behavior. This observation suggests a surface enrichment of the unreacted $[ClC_4H_8SO_3]^-$ anion at the expense of the formed chloride, which depletes into the bulk. Such a depletion of chloride has been seen before in a solution of $[Pt(NH_3)_4]Cl_2$ in $[C_2C_1Im][EtOSO_3]$ and was explained by the smaller molecular volume and the lower polarizability of chloride in comparison to $[EtOSO_3]^-$.[22] It is noteworthy, that both **IL1** and **IL2** were free of any surface impurities, such as Si impurities from dissolved silicon grease.

After investigating **IL1** and **IL2** separately, we turned to the reactive **IL1**/**IL2** mixture and to the observation of the alkylation reaction of **IL2** and **IL1** by in situ XPS. As the reaction hardly proceeds at room temperature, the binary 1:1 mixture of the reactant ILs could be prepared under ambient conditions. This mixture was transferred into the XP spectrometer within 10 minutes and then heated, while XPS data were recorded.

The Cl 2p, N 1s, O 1s, and F 1s XP spectra in 0° emission before (black) and after (red) heating the **IL1**/**IL2** mixture at 100 °C for 2 hours in the spectrometer are shown in Figure 3 (left-hand side); the corresponding C 1s and S 2p spectra are shown in Figure S3 in the Supporting Information. Upon heating to 100 °C, the Cl 2p region clearly shows an almost complete transformation ((91 ± 5) %) of covalent chlorine (Cl_{cov}; Cl $2p_{3/2}$ at 200.2 eV) to chloride (Cl_{ion}; 197.0 eV) in the near-surface region. From the Cl 2p region alone, however, discrimination between alkylation (i.e., **IL3** formation), sultone formation, and chlorobutylsulfonate ester formation is not possible, because the transformation of covalently bound Cl to chloride occurs in all cases. The required information can be derived from the N 1s region, which shows two well-separated signals: the signal at 401.9 eV is attributed to the nitrogen atoms (N_{imid}) of the imidazolium moieties of **IL1** and **IL2**, and the signal at 399.4 eV to the amine functionality (N_{amine}) of **IL2**. After heating, the N_{amine} signal intensity decreases to (44 ± 5) %, thus suggesting a (56 ± 5) % conversion of **IL2** to **IL3**. The loss in N_{amine} signal intensity is balanced by the broadening of the N_{imid} signal, which is attributed to the emerging ammonium group in **IL3**. By fitting the N 1s spectra to the three distinct nitrogen species, a binding energy of (403.1 ± 0.2) eV for this ammonium group N_{ammon} was found (see dashed line in Figure 3).

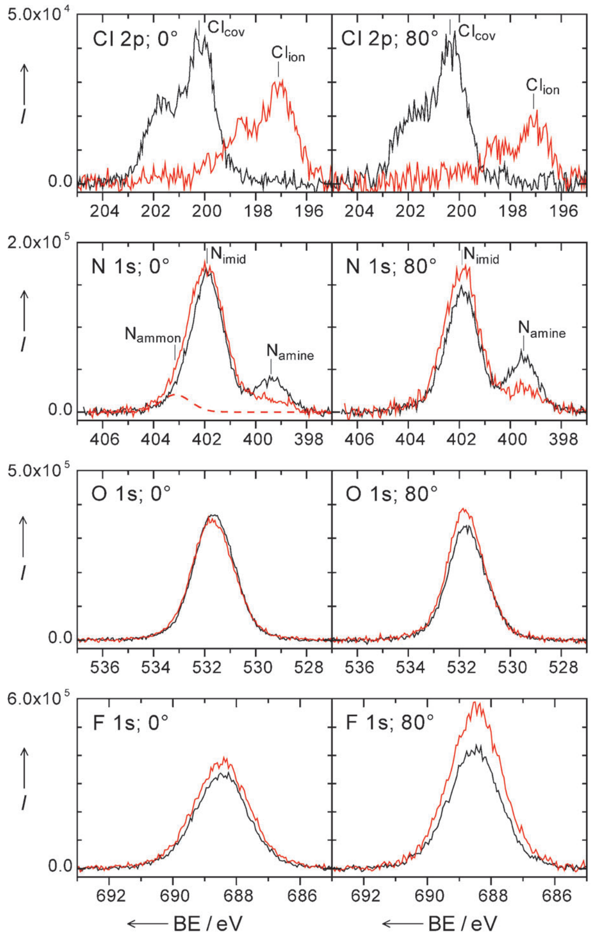


Figure 3. Detail XP spectra of Cl 2p, N 1s, O 1s, and F 1s regions of **IL1**/**IL2** mixture in 0° emission (left) and 80° emission (right) before (black line) and after (red line) heating to 100 °C for 2 hours.

To get an independent confirmation of the alkylation reaction in the spectrometer, the sample holder of the spectrometer was washed with methanol right after the above-described heating of the IL**1**/IL**2** mixture, and the collected solutions were analyzed by ESI-MS. As expected, the $m/z = 304.2$ signal in the ESI-MS analysis unambiguously proved the formation of the IL**3** cation.

The 56 % conversion of the IL**2** cation $[(Me_2NC_3H_6)C_1Im]^+$ suggests that it reacts with 56 % of the IL**1** anion $[ClC_4H_8SO_3]^-$ to form IL**3**. The additional conversion of covalent chlorine Cl_{cov} to chloride Cl_{ion} is due to sultone or ester formation. The 9 % Cl_{cov} signal left after heating (see above) indicates that 18 % of IL**1** have reacted to ester according to Scheme 2 b (note that upon ester formation two Cl_{cov} are converted to one Cl_{cov} and one Cl_{ion} species). The remaining 26 % of IL**1** are then converted to volatile sultone. As both IL**1** and IL**2** contain one SO_3 group, this should result in 13 % decrease in O 1s and S 2p intensities. However, upon heating, only minor changes ($<5\,\%$) occurred in the O 1s (Figure 3) and S 2p regions (see the Supporting Information, Figure S3). At the same time, we observed an increase of the F 1s intensity (by $(18 \pm 5)\,\%$) and a concomitant decrease in the total Cl 2p signal intensities (by $(20 \pm 5)\,\%$) in the 0° spectra in Figure 3 upon heating (note that both effects are even more pronounced at 80°). This behavior indicates a depletion of chloride from the surface-near region and a concomitant enrichment of the more surface-active SO_3-containing $[TfO]^-$ anion. This enrichment roughly compensates the loss of SO_3 groups because of the formation of volatile 1,4-butane sultone.

In conclusion, we have demonstrated that it is possible to monitor an organic liquid-phase nucleophilic substitution reaction by in situ XPS. The applied method, which is new for the investigation of organic reactions, allows to follow the fate of all elements present in the reaction mixture (except for hydrogen) in a quantitative and oxidation-state-sensitive manner and in one experiment. The general approach is to attach ionic head groups to the reacting organic molecules, in order to reduce their volatility. Herein, we investigated the nucleophilic substitution reaction between $[C_2C_1Im][ClC_4H_8SO_3]$ (IL**1**) and $[(Me_2NC_3H_6)C_1Im][TfO]$ (IL**2**). We found that the alkylation of the amine functionality of IL**2** by the 4-chlorobutylsulfonate anion of IL**1** occurs in the near-surface region with a conversion of 56 % under the applied UHV conditions. As parallel reactions, the formation of an anionic sulfonate ester and the intramolecular elimination of volatile sultone from the anion $[ClC_4H_8SO_3]^-$ have been taken into account and quantified. For future studies, it appears feasible to also investigate the kinetics of organic liquid-phase reactions by following the evolution of a particular core level over time in isothermal experiments under XPS monitoring.[23] For such measurements, the data-collection time has to be reduced either by concentrating on one core level or by using high-intensity synchrotron radiation.[23] We anticipate that the herein described new method of investigating liquid-phase organic reactions can be transferred to many other organic transformations, apart from nucleophilic substitution reactions. As XPS represents an atom-specific, oxidation-state-specific, and surface-selective analysis technique, a significant amount of mechanistically relevant information on the surface region of reacting organic systems will become accessible with this approach.

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