Ionic Liquids

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Probing a Gas/Liquid Acid–Base Reaction by X-ray Photoelectron Spectroscopy**

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One of the most fundamental issues in reaction chemistry is the identification of the reaction mechanism, possible intermediates, or by-products and the reaction kinetics. Numerous analytical methods are routinely employed to monitor the progress of reactions and to extract information on the underlying molecular mechanisms. These methods include NMR, UV/Vis, and IR spectroscopy, mass spectrometry, and calorimetric techniques. X-ray photoelectron spectroscopy (XPS) is not traditionally used for reaction monitoring, although it has the potential to complement these techniques and is even superior in certain respects.

Unlike many other spectroscopic tools, XPS is quantitative and enables direct, in situ observation of nearly all elements present in a sample, except hydrogen and helium. Changes of the chemical environment are reflected by changes in the corresponding core-level binding energy, the so-called chemical shifts. Furthermore, XPS is sensitive to the sample surface with a typical information depth at the nanometer scale. This is particularly helpful when studying heterogeneous reactions of gas-phase species with reactive surfaces. It is this interface between both reactants which mainly determines the reaction behavior. Thus, the investigation of processes at reactive interfaces is of fundamental importance.

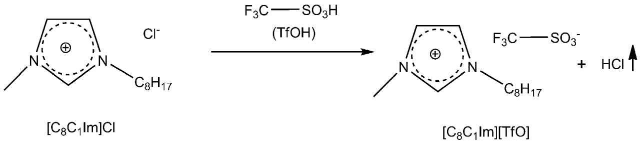
Within the last 20 years, many contributions have been made towards the understanding of reactions on catalytically active metal or metal oxide surfaces by using real-time XPS or other surface-sensitive techniques.[1–10] As most of these techniques require ultra-high vacuum (UHV) conditions, their application is restricted to solid surfaces covered with ultrathin adsorbate layers at monolayer or submonolayer coverage. Often the otherwise liquid or gaseous species remain adsorbed on the surface only at low temperatures. The investigation of macroscopic amounts of conventional liquids is impossible because of their comparatively high vapor pressure.

Ionic liquids (ILs) are an exception to this restriction, as UHV-based investigations like XPS can be performed even on macroscopic amounts at ambient or elevated temperatures.[11,12] This is possible because of their extremely low vapor pressure,[13,14] which, together with other interesting physico-chemical properties like conductivity[15] and considerable thermal stability[16] has given them a wide scientific attention within the last few decades. ILs are salts composed solely of ions, which are liquid below 100 °C.

Using ILs, we have recently shown that it is possible to make a huge step forward in the study of reactions by XPS, overcoming the restrictions to solid–adsorbate surface reactions.[17,18] We investigated a liquid-phase reaction, namely the alkylation of an amine, under solvent-free conditions in a macroscopic liquid film by tethering the reactive centers to ionic head groups, thereby combining reactivity and low volatility. Apart from monitoring the course of the reaction over time by following changes in peak intensities associated with the participating species, it was possible to identify side reactions and product yield. By using angle-resolved XPS (ARXPS) under grazing electron emission, that is, with increased surface sensitivity, molecular orientation and segregation effects at the outermost surface layers were determined.[18]

Herein, we have taken this concept one step further by investigating a Brønsted acid–base reaction of a gaseous strong acid with the anion of the ionic liquid acting as a base. Apart from extending the possibilities for XPS to study reaction and diffusion phenomena in very fast acid-base reactions at the gas/liquid interface, the applied model reaction excludes the occurrence of side reactions.

In detail, we investigated the acid–base reaction (see Scheme 1) between 1-methyl-3-octyl-imidazolium chloride ($[C_8C_1Im]Cl$) and triflic acid (TfOH). During this reaction,



Scheme 1. Reaction of $[C_8C_1Im]Cl$ with volatile triflic acid TfOH to form a new IL, $[C_8C_1Im][TfO]$, and HCl that evaporates under UHV conditions.

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a proton is transferred from TfOH to the basic chloride ion of the ionic liquid, forming HCl and a new anion, triflate ($[TfO]^-$). The reaction must be driven both by acid strength and, as it is carried out under vacuum conditions in the XPS chamber, by the differences in vapor pressure (p_{vap}(TfOH) $\approx 10^1$ hPa at 298 K,[19] p_{vap}(HCl, pure) $\approx 10^4$ hPa at 295 K).[20] Overall, because of the evaporation of the reaction product HCl, the reaction could also be classified as an anion exchange reaction, where the anion of the IL $[C_8C_1Im]Cl$ is substituted with $[TfO]^-$ to form the IL $[C_8C_1Im][TfO]$. Such a type of ion exchange reaction has frequently been used to synthesize ionic liquids with weakly basic anions from their corresponding chloride salts by addition of a strong acid.[21]

The reaction was carried out by dosing gaseous TfOH (through a leak valve connected to a reservoir with the liquid acid; see the Supporting Information for further experimental details) at room temperature onto the surface of a macroscopic film of $[C_8C_1Im]Cl$ (thickness ≈ 0.2 mm) at a TfOH partial pressure of 1×10^{-6} mbar (base pressure: 5×10^{-10} mbar). Figure 1 a shows the overall changes in an XP overview spectrum before (0 minutes) and after 170 minutes of TfOH dosage, and Figure 1 b displays all relevant core-level regions before dosing and after 80 and 170 minutes total dosage time. Prior to TfOH exposure, only the expected C 1s, N 1s, Cl 2s, and Cl 2p signals of $[C_8C_1Im]Cl$ were observed, with the expected intensities. Upon TfOH dosage, new signals emerged around 688.5, 532.0, 231.9, and 169.7 eV, which are attributed to photoelectrons emitted from the F 1s, O 1s, S 2s and S 2p orbitals, respectively, of the newly formed $[TfO]^-$ anion, along with the corresponding Auger signals. In the C 1s region, a new peak arose at 292.6 eV because of the CF_3 groups of $[TfO]^-$. At the same time, both the Cl 2s and Cl 2p signals of the chloride ion decreased in intensity.

After 80 minutes dosage, the initial Cl 2p intensity dropped down to about 50 %, and concomitantly, the signals of the triflate anion increased to about 50 % intensity of pure $[C_8C_1Im][TfO]$. This indicates that (within the information depth of XPS) about half of the Cl^- anions of $[C_8C_1Im]Cl$ reacted with TfOH to $[C_8C_1Im][TfO]$ and volatile HCl. After 170 minutes, Cl^- signals virtually disappeared in the overview spectrum, indicating nearly complete conversion of $[C_8C_1Im]Cl$ to $[C_8C_1Im][TfO]$. From the corresponding spectrum of the Cl 2p region in Figure 1 b, the remaining amount of Cl^- is quantified to ≈ 9 % of its original intensity. Since no other Cl species, such as covalently bound Cl or Cl_2 are observed in the Cl 2p region, we conclude that the proton transfer/anion exchange is the only process taking place. The calculated atom percentages of all elements after 170 minutes of TfOH dosage are—apart from a small reduction in $[TfO]^-$ signals and the additional Cl signals—in perfect agreement with the nominal values for pure $[C_8C_1Im][TfO]$ (gray spectra in Figure 1 b) within the experimental error (± 2 % in relative intensities), clearly pointing towards near completion of the reaction.

Further information can be extracted from the spectral changes of the C 1s and N 1s core levels. In the C 1s region three peaks are observed: the signal at 292.6 eV (C_{anion}) stems from the $[TfO]^-$ anion formed in the course of the reaction. The peak at 285.0 eV (C_{alkyl}) is attributed to the seven carbon atoms of the octyl chain bound to carbon and hydrogen only, and the peak at ≈ 286 eV (C_{hetero}) refers to the five carbon atoms bound to nitrogen of the imidazolium ring. The C_{alkyl}, the C_{hetero}, and also the N 1s signals solely originate from the cation of the IL, which is not involved in the acid–base reaction. Nevertheless, these signals decrease by 12–14 % after 170 minutes of dosage time. This decrease directly reflects the overall change of the IL density, because of the exchange of the small Cl^- anion by the considerably larger $[TfO]^-$ anion (molecular volumes of the neat ILs see Kolbeck et al.).[22]

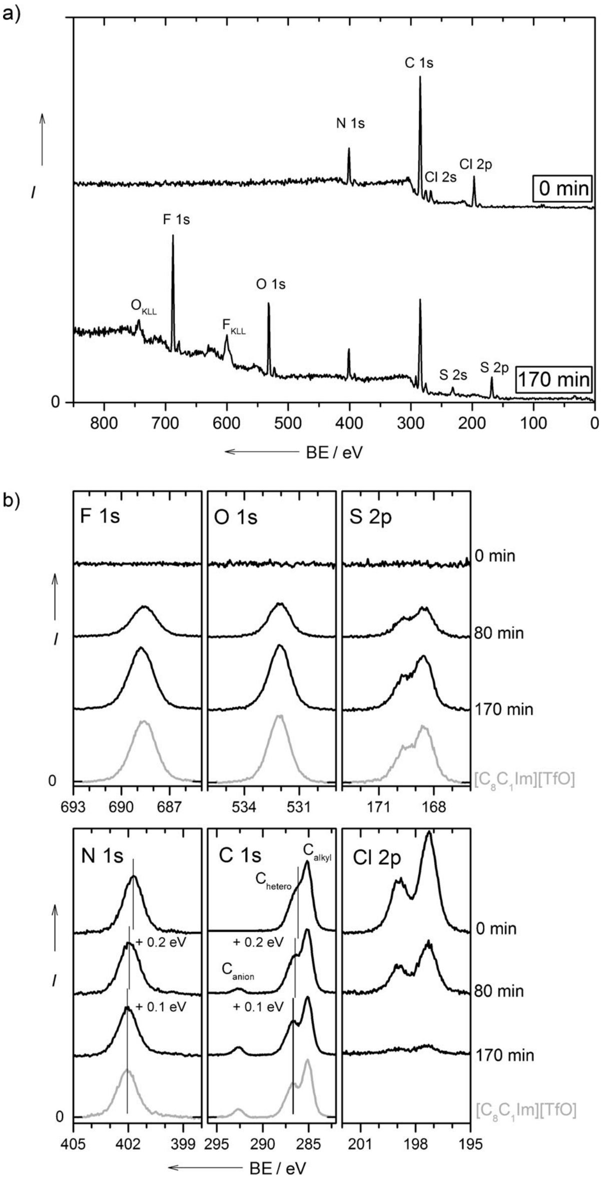

Figure 1. a) Overview spectra before (0 minutes, top) and after 170 minutes (bottom) of TfOH dosage. b) Region spectra before (0 minutes), after 80 minutes and after 170 minutes of total TfOH dosage time ($p_{TfOH} = 1\times10^{-6}$ mbar). Core-level spectra of pure $[C_8C_1Im][TfO]$ (gray) are shown for comparison. Gas dosage and XPS recording were performed at room temperature under normal emission conditions (information depth ≈ 7–9 nm).[12]

The second prominent change in the cation signals is the shift of the N 1s and C_{hetero} peaks towards higher binding energy by approximately 0.2 eV after 80 minutes of gas exposure, and by an additional 0.1 eV shift after 170 minutes total dosage time. These shifts reflect changes in the mean anionic environment of the imidazolium head group in course of the reaction. Such anion-dependent effects were systematically studied by Cremer et al.[23] The here observed N 1s and C_{hetero} peak positions for $[C_8C_1Im]Cl$ (before the reaction) and $[C_8C_1Im][TfO]$ (after the reaction) coincide with the values reported there.[23] To finally prove that the reaction product is indeed $[C_8C_1Im][TfO]$, we included the spectra of pure $[C_8C_1Im][TfO]$ in Figure 1 b (gray spectra at the bottom). It is evident that the spectra are identical to those of $[C_8C_1Im]Cl$ after reaction with TfOH. Thus, all our findings clearly demonstrate that, at least within the information depth of XPS (7–9 nm), nearly complete conversion to $[C_8C_1Im][TfO]$ has indeed taken place for this acid–base reaction.

As next step, we show that this conversion was restricted to the near surface region of the macroscopic IL film. After 170 minutes exposure time to TfOH, the reacted IL was first stored under UHV for 30 h and, thereafter, heated to 370 K for one hour to decrease viscosity and increase ion mobility. After the first step, that is, leaving the IL in UHV, the spectra remained unchanged within the margin of error (not shown). However, after heating, distinct changes occurred, as shown in Figure 2.

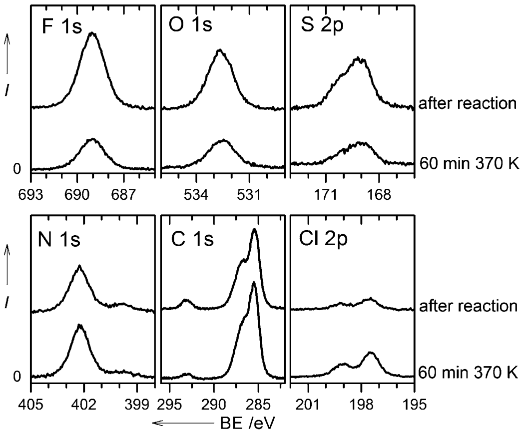

Figure 2. Comparison of core-level spectra taken under normal emission of $[C_8C_1Im]Cl$ exposed for 170 minutes to TfOH at 1×10^{-6} mbar partial pressure forming mainly $[C_8C_1Im][TfO]$ (top) and after heating the reacted IL to 370 K for 60 minutes (bottom).

The peaks attributed to the $[TfO]^-$ anion, namely F 1s, O 1s, C_{anion}, and S 2p, decreased to 47 ± 8 % of their maximum intensities and simultaneously, the Cl 2p doublet reappeared. This effect is attributed to diffusion of Cl^- anions from the IL bulk region, where no reaction with TfOH occurred under the applied reaction conditions, to the near-surface region (i.e. to within the information depth of our XPS setup of about 7–9 nm). The back reaction, that is, proton transfer to re-form Cl^- is ruled out, as the gaseous product HCl irreversibly evaporates directly upon formation and is pumped off the vacuum system. Thus, HCl liberated in the previous ion exchange cannot account for the reappearance of the chloride signals given the applied UHV conditions for a period of several hours.

In conclusion, we succeeded to monitor a Brønsted-type acid–base reaction of gaseous triflic acid (TfOH) and the basic chloride anion of the IL $[C_8C_1Im]Cl$ in situ by XPS. This gas/liquid reaction occurs at the surface of the IL and is nearly complete in the surface-near region after 170 minutes of TfOH dosage at 1×10^{-6} mbar. The progress of the reaction was deduced from the decrease of the chloride signal and by simultaneous appearance of the F 1s, O 1s, C_{anion} and S 2p signals of the triflate ionic liquid. The corresponding spectra after the reaction coincide with the spectra of pure $[C_8C_1Im][TfO]$. Furthermore, intensity changes in N 1s, C_{hetero}, and C_{alkyl} intensities reflect changes in the IL density because of exchange of the small Cl^- anion by the much more bulky $[TfO]^-$ anion. This is accompanied by changes in charge transfer from the anion to the cation in the case of $[C_8C_1Im][TfO]$ (i.e. after reaction) which can be deduced from C_{hetero} and N 1s peak shifts. Heating of the IL layer after the reaction shows a reappearance of the reactant $[C_8C_1Im]Cl$ which indicates that under the applied conditions the reaction is restricted to the near surface region, and that because of the increased ion mobility at elevated temperatures, an intermixing of $[TfO]^-$ ions at the surface with unreacted Cl^- ions from the bulk occurs.

These results constitute the first example of an in situ XPS study of a gas/liquid acid–base reaction and open a new route towards characterizing such reactions in great detail. In contrast to our earlier liquid–liquid alkylation studies,[17,18] the absence of additional side reactions and the possibility to apply one of the reactants in a well-defined manner allow detailed investigations on the reaction mechanisms, reaction kinetics, and diffusion processes, particularly in temperature-dependent experiments. In the future, angle-resolved XPS measurements will give access to additional information on the surface composition and on the orientation of the molecules at the gas/liquid interface. It is also anticipated that by comparing the reaction rate of several volatile acids with $[C_8C_1Im]Cl$ (or any other ionic liquid with a basic anion) the acidity of such acids in the corresponding ionic liquids can be determined in an indicator-free manner. Given the high importance of acidic ionic liquids and acidic IL mixtures in catalysis, such studies will be also of significant practical relevance.

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