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Dissociation of Water on the Surface of Organic Salts Studied by X-ray Photoelectron Spectroscopy

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Water dissociation has important implications for numerous chemical processes. Although extensively studied on metals and to some extent on inorganic salts, this phenomenon has not yet been shown to occur on organic surfaces. Herein, the ability of two crystalline organic hydrochloride salts to induce water dissociation at their surface was demonstrated. Using a modified X-ray photoelectron spectroscopy setup, the oxygen lacking crystalline organic salts were exposed to high water vapor pressures within an environment sealed from ambient air. Thus, the O(1s) peak resulting from exposure to water vapor at room temperature could be unambiguously assigned to dissociated water, a phenomenon previously unreported with organic material. Both powder and single crystal samples were investigated, to determine the effect of defects on the extent of dissociation. Dissociation was shown to be dependent on the level of defects present at the surface. The presence of highly reactive dissociated water on organic surfaces has important implications for the solid state chemical stability of these substances.

Introduction

Adsorption of gaseous species is often the first and most important step in reactions at solid surfaces. The abundance of water in the atmosphere renders it one of the most important adsorbates and consequently one of the most well studied. Although water has been extensively studied on metallic and inorganic surfaces,^{1–3} there is a noted absence of related work on organic surfaces. The goal of this contribution is to explore whether dissociative adsorption of water is possible on the surface of organic salts, a phenomenon unreported to date. Organic salts are important forms of drugs, vitamins, explosives, and agrochemicals, whereby the solid state properties of the compound are modified through salt formation. Understanding if water is molecularly or dissociatively adsorbed is of critical importance within many scientific fields because the presence or absence of dissociation will influence chemical reactions. The dissociated state of water is a considerably more reactive form than its molecular counterpart. Dissociative adsorption is a form of chemisorption, where interatomic bonds of the original adsorbate molecule are disrupted upon the formation of a chemical bond between surface atoms or molecules and the adsorbate via electron exchange.

Within the field of organic materials, it is well established that organic crystals typically degrade more rapidly in the presence of atmospheric moisture. Knowledge of the fundamental nature of these reactions is still sparse, particularly around contributing factors toward surface hygroscopicity and the subsequent role in initiating chemical instability. To date, there has been very limited work performed to investigate the state of water on the surface of organics via ultrahigh vacuum (UHV) surface analysis techniques, in contrast to the extensive body of work on adsorbed water

on other more stable nonorganic materials. Impartial reasons exist for the low involvement of such techniques within investigations of organic materials, particularly with adsorbed species such as water. Organic samples often exhibit high vapor pressures and degas excessively under vacuum, creating incompatibilities with the involved processes and equipment. Another reason relates to the inherent insulating properties of untreated organic materials, as surface analysis techniques often employ electrons as a probe. Finally, the water sticking coefficient typically is extremely low over a crystalline hydrophobic organic material, requiring high water exposures achieved only in an ambient (high-) pressure reaction cell, an option which is not widely available.

X-ray photoelectron spectroscopy (XPS) is a powerful surface sensitive technique that has become widely used for studying physical and chemical phenomena associated with atoms and molecules at the surfaces of solids.^{4,5} Again, investigations have mainly been limited to inorganic materials, and very few organic-relevant problems have been approached. Despite this fact, XPS is one technique frequently used to study surface water, particularly in providing evidence for dissociative adsorption of water.^{1,6,7} Additional limiting problems associated with XPS studies of organic materials exist, including possible radioactive damage to the sample and an inherently narrow C(1s) region, the most informative for organic samples, resulting in overcrowding of photoemission peaks with loss of information.

The O(1s) core-level binding energy (BE) for molecularly adsorbed water on the surfaces of metals, metal oxides, and semiconductors is normally in the range of 533–535 eV,¹ while lower BEs are indicative of the dissociated species (530–532 eV). Furthermore, molecularly adsorbed water is normally only observed if the sample is analyzed at cryogenic-like temperatures; at ambient temperature, molecularly adsorbed water will desorb

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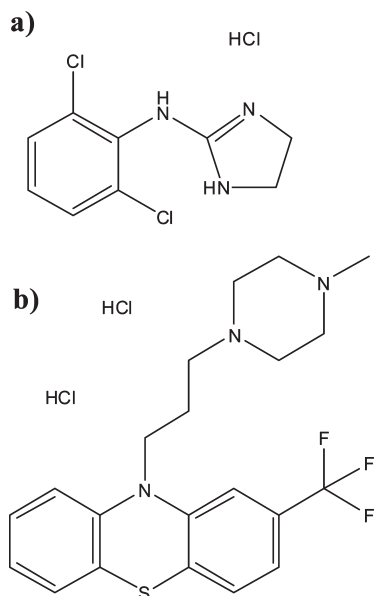


Figure 1. Molecular structures of (a) clonidine hydrochloride and (b) trifluoperazine dihydrochloride.

under UHV conditions. Detection of the O(1s) signal for a non-oxygen-containing surface provides compelling evidence for the presence of dissociated hydroxyl groups.

Selection of a model compound was extremely critical for this work, due to the aforementioned problems associated with organic compounds, as well as the likelihood of interference from molecular oxygen in the O(1s) region of the XPS spectra based on initial experiments with oxygen-containing compounds. The criteria of foremost importance pursued in selection of model compounds were as follows:

- crystalline inorganic salt of an organic free base of sufficient chemical complexity to be representative of relevant classes of fine chemicals of interest, for example, pharmaceuticals and agrichemicals
- no molecular oxygen atoms to eliminate the possibility of interference with the O(1s) XPS signal of adsorbed water species
- stable under both ultrahigh vacuum and high temperature conditions
- stable under X-ray radiation

Stronger crystalline intermolecular binding generally translates to diminished susceptibility to phase change and improved chemical stability; the risk of localized heating induced by the X-ray beam thus compelled the inclusion of melting point as a crucial prescreening consideration in the selection of possible compounds. A series of potential compounds were screened by exposing the compounds to high vacuum conditions within the load-lock chamber of the XPS instrument to test their propensity to degas. Sufficiently nonvolatile compounds were tested subsequently for stability under high temperatures and upon exposure to the X-ray beam. The two model compounds chosen were trifluoperazine (10-[3-(4-methylpiperazin-1-yl)propyl]-2-(trifluoromethyl)-10H-phenothiazine) dihydrochloride (mp 242 °C), an antipsychotic agent, and clonidine (*N*-(2,6-dichlorophenyl)-4,5-dihydro-1H-imidazol-2-amine) HCl (mp 305 °C), an α -adrenergic agonist, whose structures are depicted in Figure 1.

The objectives for this study are twofold: (1) to detect and confirm the apparent dissociation of water on the surface of organic salts using a modified XPS setup for exposure of samples

to contaminant-free moisture, and (2) to investigate the properties of the substrate that lead to the dissociation of adsorbed water. The hypothesis is that organic hydrochloride salts (and possibly other types of organic salts) containing surface defects will promote the chemical dissociation of water.

Experimental Materials and Methods

Methods. *X-ray Photoelectron Spectroscopy Instrumentation.* XPS data were obtained by using a Kratos Ultra DLD spectrometer using monochromatic Al K α radiation ($h\nu = 1486.58$ eV). The atomic concentrations of the chemical elements in the near-surface region were estimated after the subtraction of a Shirley type background, taking into account the corresponding Scofield atomic sensitivity factors and inelastic mean free pass (IMFP) of photoelectrons. The binding energy (BE) values referred to the Fermi level were corrected using the C 1s 284.80 eV; the standard deviation of the peak position associated with the calibration procedure was ± 0.05 eV. A commercial Kratos charge neutralizer was used to achieve a resolution of 1.0–1.2 eV measured as a full width at half maximum (fwhm) of the C 1s deconvoluted peaks. The XPS spectra were fitted by CasaXPS software assuming line shape to be a Gaussian–Lorentzian function.

Experimental Setup for Exposure to Moisture. Since modification of existing commercial XPS instrumentation was vital to achieve the conditions necessary for appropriate substantiation of the phenomenon under investigation, some description of the experimental setup is provided here. Presentation of samples absent of pre-experimental exposure to ambient air was achieved by developing and employing a modified load-lock chamber (LC) of the existing XPS instrument. This external chamber is separated from the analysis chamber by an exchange chamber, where each of the chambers is individually pumped down to ultrahigh vacuum conditions. Briefly, the LC was fitted with an inlet gas line from a relative humidity generator (RH-200, VTI Corporation) operated with dry nitrogen gas. Following exposure within the LC followed by pumpdown, samples could be directly transferred pre- and postexposure to moisture through the series of chambers to the analysis chamber, remaining under vacuum ($< 1 \times 10^{-5}$ mbar). Both the LC and analysis chamber were equipped with cooling and heating capabilities as well to allow variable temperature experiments in the range of 110–400 K. The LC was fitted with a wobble stick and attached blade for cleaving of single crystals under high vacuum conditions. Single crystals were fixed in place between two adjustable copper plates which were secured by screws into the sample holder. Either gold foil (0.05 mm thick, 99.95%, Alfa Aesar, Ward Hill, MA) or strips of ultrahigh-vacuum-compatible copper tape (double coated, SPI Supplies Division of Structure Probe, Inc., West Chester, PA) were used as a buffer between the copper plate and crystal to aid in secure fastening while preventing excessive pressure capable of fracturing the crystal. The sample holder was gold-plated to prevent oxidation on its surfaces.

Scanning Electron Microscopy (SEM). SEM images were obtained using a JEOL JSM-840 scanning electron microscope (JEOL USA Inc., Peabody, MA) equipped with a secondary electron detector and a tungsten filament source. For these experiments, the samples were sputter-coated using Au–Pd to alleviate charging.

Results

Initial analyses with both clonidine HCl and trifluoperazine di-HCl salts revealed minimal X-ray damage postanalysis. Powder samples were found to have greater susceptibility to X-ray beam damage upon repeated analysis of a single sample; therefore, separate samples were analyzed following each respective treatment. Powder samples of the two salts subjected to elevated relative humidities in ambient air were initially analyzed, in order

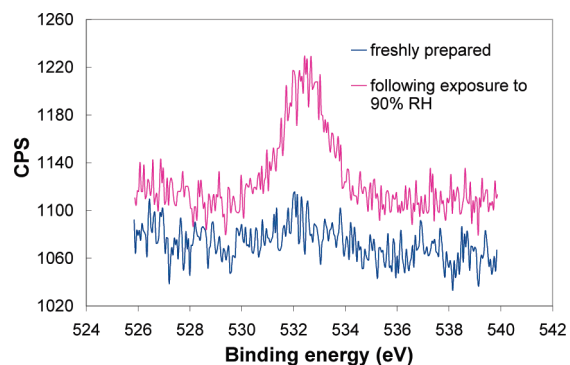


Figure 2. O(1s) photoelectron spectra of a freshly prepared powder sample of clonidine HCl, before and after exposure to moisture (90% RH).

to determine whether evidence for dissociated surface water exists. For clonidine HCl, initial studies on a powder sample stored at 25 °C/51% RH for 24 h showed an O(1s) peak at a binding energy of 531.9 eV, with an elemental composition of 1.8%. Preliminary experiments with a powder sample of the second organic salt, trifluoperazine dihydrochloride (TFP), exposed to conditions of 25 °C/51% RH for 24 h, showed an O(1s) peak at a binding energy of 531.9 eV. Based on the binding energies observed, these results are consistent with the presence of dissociatively adsorbed water.

In order to minimize the existence of pre-experimental water species or oxygen-containing impurities, freshly prepared powder samples of clonidine HCl were analyzed. Clonidine HCl single crystals were ground in a mortar and pestle and transferred immediately to the LC for pumpdown. Analyses of multiple samples were unable to yield spectra completely free of an initial O(1s) peak. However, analysis following subsequent exposure to 90% RH for 1 h within the LC showed that the elemental % of likely dissociatively adsorbed water, based on the O(1s) peak, increased significantly. The results of one such experiment are shown in Figure 2, where the BE of the O(1s) peak occurred at 532.2 eV. No loss of the dissociated form was observed upon increasing temperature up to 413 K, and a consistent BE of 532 eV was observed. Molecular water was observed during a similar experiment as described above, performed with a single RH exposure followed by immediate cooling of the sample to 110 K after pumpdown. The water species was discerned by both the BE of the O(1s) peak at 533.5 eV and its desorption upon equilibration of the sample at room temperature.

Single Crystal Experiments with Clonidine HCl. Clonidine HCl was chosen for subsequent single crystal experiments, due to its ability to be grown as large (> 1 mm) six-sided columnar crystals. For this work, the [100] face was used for the single crystal experiments. The crystals cleaved with ease parallel to this face, and cleaving was achieved with a stainless steel blade. Experiments were performed with crystals cleaved both in ambient conditions and within the modified LC under vacuum, and they are noted accordingly in the text. Since the sample holder surfaces are subject to ambient air preloading, the potential for the presence of oxygen-containing contaminants or oxidation on these surfaces exists. To minimize this possibility, gold foil served as a buffer between the sample holder parts and the single crystals during cleavage and analysis. Obtaining completely flat cleaved faces was impossible, as both pre- and post-XPS analyses with SEM revealed fairly defective surfaces largely in the form of steps.

Single Crystal Experiments with Post-SEM. In order to investigate the effect of surface defects on the extent of dissociation, two single crystals were cleaved in ambient conditions and

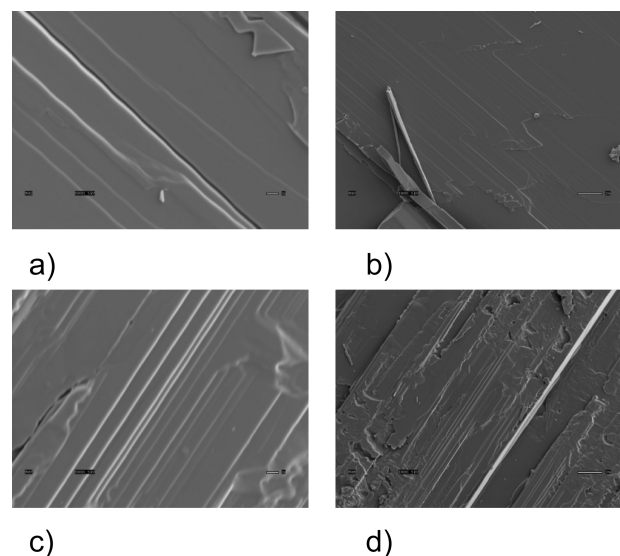


Figure 3. SEM images of cleaved [100] faces of clonidine HCl: sample 1 at (a) 5000 \times and (b) 1000 \times ; sample 2 at (c) 5000 \times and (d) 1000 \times .

Table 1. Elemental Compositions (%) of O(1s) at 532 ± 0.2 eV for Freshly Cleaved Samples of the [100] Face of Clonidine HCl, before and after Exposure to 90% RH within the LC^a

initial	O(1s) %
[100] sample 1	0.41
[100] sample 2	0.46
after exposure to 90% RH for 1 h	O(1s) %
[100] sample 1	3.42
[100] sample 2	7.53
defect density	steps/ μ m
[100] sample 1	0.6
[100] sample 2	1.1

^aSample numbering corresponds to SEM images in Figure 3. Included are values of defect density based on SEM images.

transferred immediately to the LC followed by pumpdown. Initial analysis revealed the presence of an O(1s) peak, with a BE consistent with the earlier results suggesting dissociated water. Following analysis of the two samples (samples 1 and 2), exposure at 90% RH within the LC was performed. Subsequent analysis showed large increases in the elemental % of oxygen from the O(1s) peak, and again the binding energies were consistent with previous experiments (532.0 ± 0.2 eV). Scanning electron microscopy images of the analysis regions of the two cleaved single crystal samples were collected post-XPS. Sample 2 showed greater amount of defects/steps, as is evident from images of the two sample surfaces depicted in Figure 3. Estimates of the observable step density (steps/distance) for sample 2 were approximately twice that of sample 1 (see Table 1). A correlation is readily observable whereby the greater defect density of sample 2 corresponds with a larger increase in the quantified level of dissociated water detected following exposure (Table 1).

In order to investigate a presumably “clean” face, precluding the presence of initial water or oxygen-containing species, a single crystal sample of clonidine HCl was cleaved along the [100] face under high vacuum ($\sim 1 \times 10^{-7}$ mbar) within the LC. The sample was immediately (within 30 s) transferred into the sample exchange chamber, with a pressure of approximately 8×10^{-10} mbar

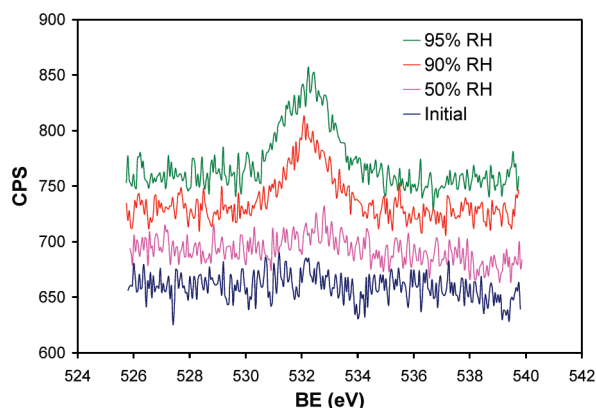


Figure 4. O(1s) photoelectron spectra of a cleaved [100] face of a clonidine HCl single crystal, analyzed initially then following exposure to increasing RH.

immediately before transfer. The sample was transferred repeatedly between the analysis and load-lock chambers, analyzing initially postcleavage and again following exposures to 50%, 90%, and 95% RH, each for approximately 90 min within the LC. No evidence of an O(1s) peak was observed in the initial XPS spectrum, as depicted in Figure 4. Although other experiments with freshly prepared samples had on occasion detected noticeable O(1s) peaks nearly within the associated noise, the vacuum-cleaved sample showed no detectable peak. However, following exposure at 50% RH, a noticeable O(1s) peak appeared in the BE region indicative of the dissociatively adsorbed species at approximately 532 eV, and substantially elevated levels of the species were found after exposures to 90% and 95% RH (see Figure 4).

Discussion

We have provided compelling evidence that dissociative adsorption can occur on defective surfaces of organic salts of inorganic acids. This is based first on the binding energy of the observed O(1s) peak associated with exposure to moisture, appearing consistently at approximately 532 eV in our results. A control experiment with a previously unexposed crystalline clonidine HCl surface, prepared by cleavage within the load-lock chamber under vacuum, showed no initial presence of oxygen but demonstrated increasing amounts of dissociative adsorption with exposure to higher water vapor pressures. Of foremost importance, the setup utilized was designed to exclude any exposure to ambient air and consequential contribution of other oxygen-containing species to the O(1s) peak, as well as the possibility of impurity-induced dissociation. The binding energy of molecular water at 110 K on the surface of trifluoperazine di-HCl was found to be 533.5 eV, while the dissociated form of water showed no change in BE upon cooling to the same temperature. Furthermore, the subsistence of dissociatively adsorbed water at 413 K supports existence of a chemisorbed species, differentiated from physisorption by the strength of the adsorbate–substrate interactions. The process either is irreversible or requires elevated temperatures to those studied here for desorption to occur.

Salt surfaces are generally considered to be inert toward dissociation.¹ While dissociation occurs for metals and metal oxides even on defect-free surfaces, only molecular water has been observed on ideal, defect-free alkali halide surfaces. However, recent evidence suggests defects on inorganic salt surfaces may induce dissociation, with less certainty around the specific mechanism. For instance, it has been shown that dissociation may occur at F centers, which are produced by missing negative ions. These may be replaced by ions

such as OH[−] stemming from dissociation of water. Even at pressures as low as 10^{−6} Torr at room temperature, surface defects may serve as active sites for adsorption of water molecules on NaCl surfaces, with chemisorption and dissociation occurring on F centers.⁸ Malaske et al.⁹ observed by near-edge X-ray absorption fine structure (NEXAFS) studies that electron bombardment of high quality single crystalline thin films of NaCl(100) resulted in OH[−] formation at F centers, while at the defect-free surface only molecular water is adsorbed. Recent Fourier transform infrared (FTIR) studies have shown that water adsorbs on the surfaces of NaCl(100) crystallites at room temperature and dissociates at defect sites.¹⁰

Our findings are consistent with results on sodium chloride surfaces where it is believed the phenomenon is defect-induced.^{10–12} Analogously to this inorganic surface, defects on the surface of organic hydrochlorides might be expected to be active to dissociation. Although the surfaces of prepared powder samples are expected to have a large number of defects, the results here indicated that the cleaved single crystal surfaces have comparable levels of defects capable of inducing water dissociation at the surfaces studied. Some of the most frequently observed forms of defects include steps, kinks, voids, or edges. Imaging by SEM showed high populations of steps on the surface of single crystals of clonidine HCl, suggesting these are largely responsible for the activation of this phenomenon. Ghosal and Hemminger,¹² in their investigations on the effect of grinding on the nature and content of surface adsorbed water on NaCl, analyzed three different types of freshly prepared samples. Ground powder samples and crystallites had significantly more surface defects than a freshly cleaved NaCl[100] surface. Based on the O(1s) photoelectron spectra for the sample, the powder showed considerably higher amounts of OH[−] species relative to the crystallites, while the single crystal showed essentially no surface water. Following exposures to higher humidities, further buildup of this strongly adsorbed water occurred, while shifting to higher binding energies more characteristic of molecular water. Thus, not only was the presence of defective surfaces shown to enhance the dissociative adsorption of water on the surface, but further sorption was suggested to be associated with clustering around the dissociated species. In contrast to this case, the cleaved [100] face of clonidine HCl single crystals investigated here exhibited significant levels of defects and were shown to be chemically active for dissociative adsorption.

Various mechanisms for defect-induced dissociation have been proposed for other types of materials, often associated with the structural environment of the adsorbed water. On the surface of metal oxides, dissociation must involve a cation site to bind the oxygen atom of a water molecule and an anion site to abstract a proton.¹ The geometric arrangement as well as the inherent properties of the cation and anion are believed by some authors to be determining factors; in such cases, the presence of defects may enable more favorable structural arrangements. The results obtained in this study provide compelling evidence that defect induced dissociation can also occur on a previously unexplored class of material, organic salts, based on a number of experiments and a rigorous experimental setup. The increase in the extent of the O(1s) peak observed with increasing water vapor partial

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pressure on the single crystal surface of clonidine HCl, cleaved under high vacuum, suggests an increase in the number of occupied sites which are energetically favorable for dissociation with increasing relative humidity.

Conclusions

The ability of defects on the surface of organic salts to induce dissociation of water adsorbed at high vapor pressures and ambient temperature has been demonstrated. This represents, to the best of our knowledge, the first time this phenomenon has been reported for an organic surface. Further work is needed to elucidate the mechanistic role of defects in water adsorption and dissociation at the surface of organic salts, in particular the possible effect of face chemistry at steps on the phenomenon. In addition to its reactive nature which may contribute to the

well-known instability of organic materials on exposure to humid atmospheres, dissociated water may serve as nuclei for further water uptake, with these results providing a fundamental basis for the correlation between defects and moisture affinity for this class of material. Water molecules are expected to cluster around the high polarity surface OH^- through formation of hydrogen bonds; surface hydroxides have been shown to produce a more hydrophilic surface with enhanced adsorption.¹³ Finally, the novel XPS methodology implemented in this work was successfully demonstrated to serve as a valuable tool for investigating adsorbed water species on the surface of crystalline organic compounds.

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