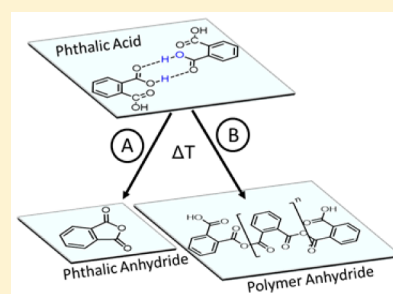


## Temperature-Dependent Reactions of Phthalic Acid on Ag(100)

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**ABSTRACT:** We have investigated the adsorption and temperature-dependent reactions of phthalic acid on Ag(100), in the temperature range 110–700 K, by synchrotron radiation X-ray photoelectron spectroscopy (SR-XPS), temperature-programmed desorption (TPD) and near-edge X-ray absorption fine structure (NEXAFS). Phthalic acid adsorbs intact at 110 K, but decomposes to phthalic anhydride and polyanhydride at 150 K. When heated further, phthalic anhydride desorbs at 250 K, leaving only polyanhydride on the surface, which at 350 K decomposes into a carboxylate, through desorption of phthalic anhydride and water. The carboxylate is stable until 500 K, after which it decomposes, through desorption of CO<sub>2</sub> and benzene, into carbon; the latter diffuses into the bulk, leaving only a little carbon on the Ag(100) surface at 600 K.



## INTRODUCTION

Silver is a well-known catalyst for many mild oxidation reactions, such as the oxidation of ethylene to ethylene oxide<sup>1</sup> and the production of formaldehyde from methanol.<sup>2</sup> As such, the adsorption and decomposition of oxygenated organic molecules on silver surfaces is of general interest, since it will offer insight into the reaction mechanism on the silver catalyst. Along with copper and gold, silver is also a popular substrate for the self-assembly of large organic molecules, which is typically studied by STM. Especially, carboxylic acid-functionalized molecules are popular, since the number and positions of the acid groups can be used to generate a wealth of ordered structures at room temperature.<sup>3–10</sup> In many cases, the assumption is made, often without clear spectroscopic evidence, that the structures at low temperature are held together by hydrogen bonds between acid groups of adjacent molecules and at elevated temperature by bonding between deprotonated carboxylate groups.<sup>5,7–9</sup> On the basis of the behavior of phthalic acid on Ag(100), we propose another possibility, namely that some of those structures might be held together by anhydride bonds instead.

## EXPERIMENTAL SECTION

Synchrotron radiation based X-ray photoelectron spectroscopy (SR-XPS) experiments were performed at the Materials Science beamline at Elettra in Trieste, Italy. They were combined with

temperature-programmed desorption (TPD) and monochromatized X-ray photoelectron spectroscopy (XPS), carried out in our home laboratory in Erlangen.

The end-station of the Materials Science beamline has a base pressure of  $2 \times 10^{-10}$  mbar and is equipped with a SPECS Phoibos 150 hemispherical energy analyzer. Core level spectra of the C 1s, O 1s, and Ag 3d regions were acquired at 380, 650, and 480 eV incident photon energy, respectively, and were measured at an emission angle of 0° with respect to the surface normal. The binding energy positions of the features in the SR-XP spectra were aligned with those measured by the laboratory source, for which the binding energy was referenced to the Fermi edge of Ag(100) ( $E_B = 0$ ). Carbon K-edge near-edge X-ray absorption fine structure (NEXAFS) spectra were acquired following the carbon KLL auger peak intensity as the photon energy was varied between 277 and 320 eV. Grazing and normal incidence NEXAFS spectra were measured at 80° incidence/20° emission and 0° incidence/60° emission relative to the surface normal, respectively.

The ultrahigh vacuum chamber at the University of Erlangen-Nürnberg has a base pressure below  $4 \times 10^{-10}$  mbar and is equipped with a Scienta ESCA 200 spectrometer (mono-

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chromatized Al  $K_{\alpha}$  X-ray source and SES 200 electron analyzer) and a Pfeiffer HiQuad QMA 400 quadrupole mass spectrometer. For TPD measurements, a homemade copper Feulner Cup was mounted around the mass spectrometer and approached to within 1 mm of the single crystal surface to increase the sensitivity. During the measurements, the Feulner-Cup was heated to 330 K to prevent a broadening of the TPD features, due to adsorption and slow desorption from the walls of the cup.

The coverages measured by SR-XPS and XPS are always referenced to the saturation coverage of phthalic acid on Ag(100) at room temperature, which we define as 1 ML. The Ag(100) single crystal (Surface Preparation Laboratory, 6 N) was cleaned by consecutive cycles of 30 min  $\text{Ar}^+$ -sputtering at 0.8 keV and subsequent annealing to 700 K for 20 min, prior to each experiment. The cleanliness was checked by SR-XPS and XPS. Phthalic acid (Sigma-Aldrich,  $\geq 99.5\%$ ) was evaporated from a radiatively heated graphite crucible held at 400 K at a rate of 0.5 ML/min. Phthalic anhydride (Sigma-Aldrich,  $> 99\%$ ) was evaporated from the same evaporator held at room temperature.

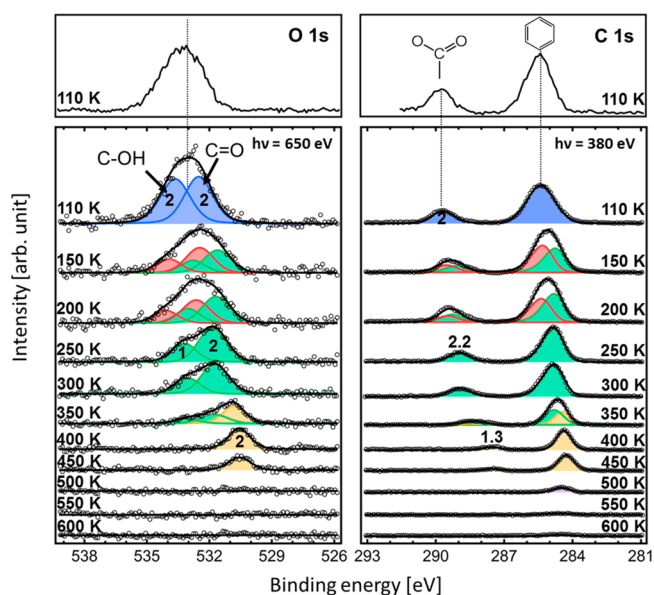
For both synchrotron and laboratory measurements, the temperature was monitored by K-type thermocouples in direct contact with the Ag(100) sample. For the laboratory measurements, the thermocouple wires were mounted into a hole in the side of the Ag(100) crystal, giving a very accurate temperature reading. However, for the synchrotron measurements the thermocouple wires were thicker and were instead simply touching the back of the Ag(100) crystal, resulting in a worse contact and a slight underestimation of the temperature. This will become apparent in the Results and Discussion section.

## RESULTS AND DISCUSSION

Figure 1 shows O 1s and C 1s SR-XP spectra of 0.5 ML of phthalic acid on Ag(100), deposited at 110 K, and heated stepwise to the indicated temperatures for 2 min each. All spectra were acquired at low temperature. Al- $K_{\alpha}$  reference XP spectra for pure phthalic acid (8 ML on Ag(100)) are displayed on top. The binding energies of the reference spectra have been shifted to correct for the reduced final state screening in the multilayer in order to align the low binding energy C 1s peak to that of the submonolayer SR-XP spectrum recorded at 110 K.

Both O 1s and C 1s SR-XP spectra at 110 K are almost identical to the reference XP spectra of the phthalic acid multilayers. The O 1s spectrum can be described by two components with a 2:2 ratio, assigned to hydroxyl oxygen at 533.6 eV ( $\text{C}-\text{O}-\text{H}$ ,  $\text{fwhm} = 1.73$  eV), and carbonyl oxygen at 532.5 eV ( $\text{C}=\text{O}$ ,  $\text{fwhm} = 1.61$  eV).<sup>6,10</sup> This 2:2 ratio is expected for the intact carboxylic acid group. The relatively small binding energy splitting between the two components points toward strong hydrogen bonds between adjacent carboxyl groups.<sup>11</sup> The C 1s spectra show two peaks at 285.4 and 289.7 eV, which are assigned to the benzene carbon atoms and the carboxylic carbon atoms, respectively, with the expected intensity ratio of 6:2. From the O 1s and C 1s spectra, we therefore conclude that the species on the surface at 110 K is intact phthalic acid.

Upon heating, three stable plateaus can be observed in both the O 1s and C 1s spectra. The first is from 150 to 200 K, the second from 250 to 300 K and the third from 400 to 450 K. For the first plateau at 150–200 K, the spectra seem to result from the superposition of two surface species, as deduced from a broadening, shift and a change of overall line shape of the O 1s

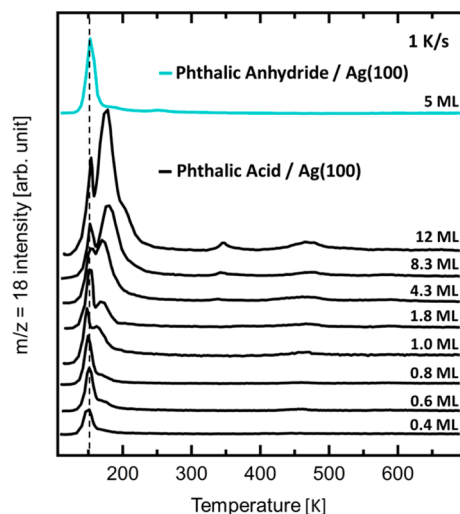


**Figure 1.** O 1s and C 1s SR-XP spectra of 0.5 ML phthalic acid deposited on Ag(100) at 110 K and heated, stepwise, to 600 K. The open circles represent the raw data after Shirley-background subtraction. Blue indicates intact phthalic acid, red polyanhydride, green phthalic anhydride, and orange a surface carboxylate. On the top, Al  $K_{\alpha}$  multilayer spectra of phthalic acid on Ag(100) are depicted as a reference.

signal and the asymmetry of the C 1s peak for the carboxylic carbon ( $\text{O}-\text{C}=\text{O}$ ) at 289.3 eV (the origin of these changes will be discussed below).

For the second plateau at 250–300 K, the asymmetry of the carboxylic C 1s peak has vanished, and the O 1s spectrum can be described by two components in a 1:2 ratio. The ratio of oxygen to carboxylic carbon has, furthermore, changed from 4:2 (fixed ratio for phthalic acid) to 3:2.2, indicating that the surface species at 250–300 K has one oxygen atom per molecule less than the species at 110 K. Diacids, such as phthalic and maleic acid, are known to easily decompose into anhydrides when heated, and both of the above observations are in agreement with the formation of an anhydride. We, therefore, label the two oxygen species as the bridging oxygen, at 533.2 eV ( $\text{C}-\text{O}-\text{C}$ ,  $\text{fwhm} = 1.38$  eV), and carbonyl oxygen, at 531.8 eV ( $\text{C}=\text{O}$ ,  $\text{fwhm} = 1.55$  eV), of an anhydride. The C 1s binding energy positions for anhydrides are very similar to those of carboxylic acids<sup>12–14</sup> and in agreement with the peaks we observe at 289.0 eV for carboxylic carbon ( $\text{O}-\text{C}=\text{O}$ ,  $\text{fwhm} = 1.1$  eV) and at 284.9 eV for benzene carbon ( $\text{fwhm} = 1.1$  eV). We therefore conclude that the surface species observed between 250 and 300 K is an anhydride.

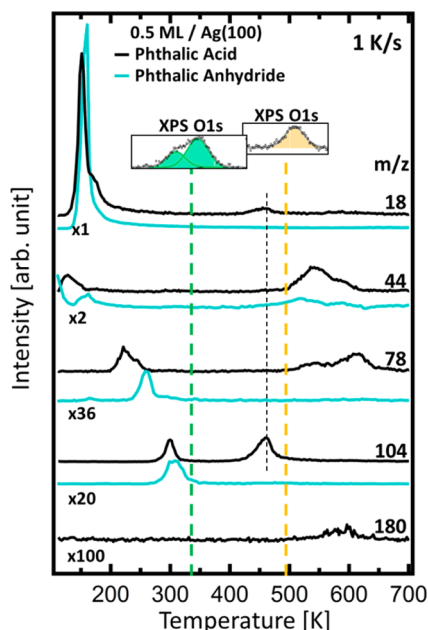
As anhydride is formed, water should be released. Figure 2 displays the TPD spectra of mass 18 (water) for phthalic acid deposited on Ag(100) at 110 K. For comparison, we also measured the corresponding TPD spectrum for phthalic anhydride, where no water formation is expected upon heating (top spectrum). The main desorption features for the phthalic acid-covered surface are a peak at 150 K and a high temperature shoulder at 170 K that, at high coverages, develops into the dominating peak. The peak at 150 K is observed for all coverages and is also present in the phthalic anhydride reference spectrum. We therefore assign this peak to residual water in the UHV chamber adsorbed on the surface below 150 K. The second peak at 170 K, which increases with phthalic



**Figure 2.** TPD spectra of water ( $m/z = 18$ ) from phthalic acid deposited on Ag(100) at 110 K at a heating rate of 1 K/s. For comparison, the topmost spectrum shows the corresponding spectrum of phthalic anhydride, also deposited at 110 K.

acid coverage, is consistent with the formation of anhydride, which remains on the surface, and water, which immediately desorbs. The two additional, small desorption peaks, at 345 and 460 K, will be discussed later.

If phthalic anhydride is formed on the surface, then it might later desorb, which should produce a signal observable in TPD. Figure 3 shows the desorption of masses ( $m/z$ ) 18 (water), 44 ( $\text{CO}_2$ ), 78 (benzene), and 104 (phthalic anhydride) after deposition of 0.5 ML phthalic acid (black) and 0.5 ML phthalic anhydride (blue) on Ag(100). Mass 104 was chosen for



**Figure 3.** TPD spectra of water ( $m/z = 18$ ),  $\text{CO}_2$  ( $m/z = 44$ ), benzene ( $m/z = 78$ ) and phthalic anhydride (fragment with  $m/z = 104$ ) from 0.5 ML phthalic acid (black lines) and 0.5 ML phthalic anhydride (blue lines) on Ag(100) at 1 K/s.  $m/z = 180$  is an unknown component with very low intensity. The numbers on the right side of the spectra indicate the magnification. The vertical green and yellow lines indicate the temperatures of the O 1s XP spectra in the insets.

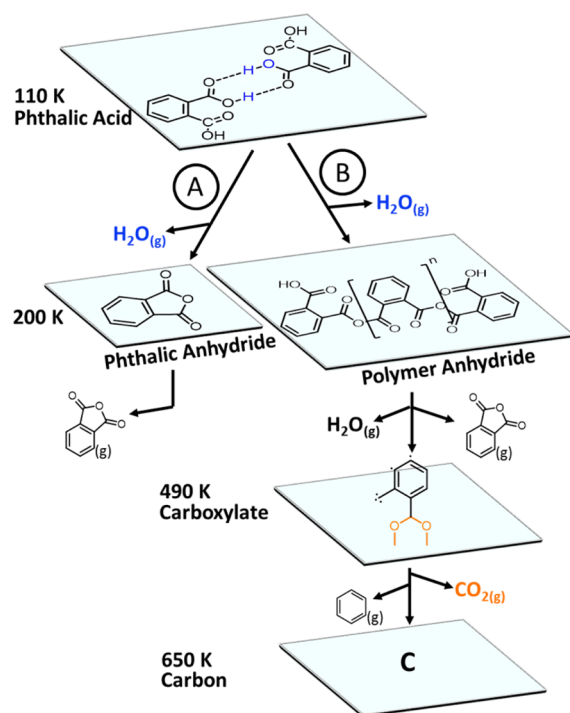
phthalic anhydride because it was the most intense fragment. The displayed masses represent all species found to desorb in the  $m/z = 1$ –300 range, apart from known cracking patterns of the identified species. Mass 180 belongs to a species with very low intensity that we were not able to identify. No desorption of hydrogen ( $m/z = 2$ ), CO ( $m/z = 28$ ), and phthalic acid ( $m/z = 166$ ) was observed.

The TPD spectra after deposition of phthalic acid (black curve in Figure 3) clearly show desorption of phthalic anhydride ( $m/z = 104$ ) at 300 and 450 K, supporting the idea of anhydride formation. The 300 K desorption peak is almost identical to the desorption peak observed when phthalic anhydride is deposited directly on the Ag(100) surface (blue curve in Figure 3). We therefore conclude that the 300 K peak is caused by adsorbed phthalic anhydride produced from phthalic acid on the Ag(100) surface. Interestingly, the 450 K peak is absent for the phthalic anhydride-covered surface; it must therefore be the decomposition product of another species.

At this point, it is important to note that we cannot directly compare the temperatures of the SR-XPS data and the TPD measurements. The SR-XPS experiments were collected at low temperature after annealing at the denoted temperatures for 2 min, whereas the TPD spectra were acquired with a 1 K/s heating ramp. Furthermore, the thick thermocouples for the SR-XPS experiments with the less than optimal contact to the sample are likely to underestimate the true sample temperatures (see the Experimental Section); thus, the temperatures indicated in Figure 1 are lower than the actual temperatures. To allow for a direct comparison, we, therefore, performed additional TPD experiments, where we stopped the heating rate at 330 and 495 K (green and orange vertical lines in Figure 3), cooled back down immediately, and measured the O 1s XP spectra that are shown as insets in Figure 3. The comparison with the XP spectra in Figure 1 shows that the spectrum after heating to 330 K in Figure 3 corresponds to the second plateau in Figure 1 (250–300 K) and the spectrum after heating to 495 K to the third plateau in Figure 1 (400–450 K).

Since the TPD spectra show desorption of phthalic anhydride already at 300 K, the species characterized by the O 1s spectra in the inset in Figure 3 after heating to 330 K (which corresponds to the second plateau from 250–300 K in Figure 1) cannot be phthalic anhydride. Nevertheless, the relative intensities of the C 1s and O 1s peaks point to an anhydride. This apparent puzzle can be solved as follows: It is reasonable to assume that phthalic acid molecules at 110 K form hydrogen-bonded networks on the surface. Thereby, the acid groups of adjacent molecules will be in close proximity, and we thus propose that the anhydride reaction not only occurs between the two acid groups within the phthalic acid molecule, but also between acid groups of adjacent molecules. This leads to the formation of dimeric and polymeric anhydride. Polyanhydrides are water-soluble polymers, which are used, for example, for drug delivery within the body. They are synthesized by melting a diacid under vacuum.<sup>15</sup> In XPS, polyanhydrides look identical to monomer anhydrides,<sup>16</sup> but the desorption temperature should be much higher. These considerations would be consistent with the species we observe after heating to 330 K in Figure 3 (during the second plateau in Figure 1). We therefore believe that the initial anhydride formation taking place (between 110 and 150 K in Figure 1) produces both monomeric phthalic anhydride and polyanhydride on the Ag(100) surface, see Figure 4. During this



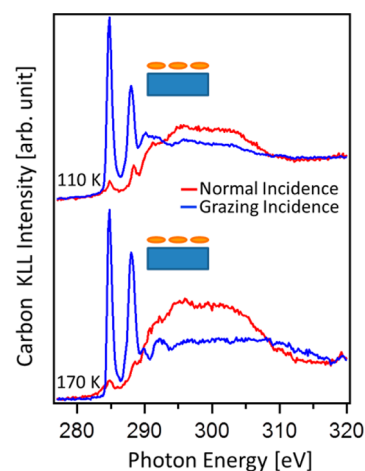


**Figure 4.** Proposed reaction scheme for the temperature-dependent reactions of phthalic acid on Ag(100).

reaction, the carbon coverage (the integrated C 1s intensity) remains essentially constant. At 300 K in Figure 3 (that is between the first and second plateaus (200–250 K) in Figure 1), the monomeric phthalic anhydride desorbs, leaving polyanhydride behind, and the carbon coverage decreases from 0.5 to 0.3 ML. This is in agreement with both the O 1s and C 1s spectra of the first plateau (150–200 K) in Figure 1, which can be described as the polyanhydride species from the second plateau (green) in addition to a second anhydride (phthalic anhydride, red). In the O 1s region in Figure 1, the red components consist of two features at 533.9 eV (fwhm = 1.37 eV) and 532.5 eV (fwhm = 1.55 eV); the splitting and ratio (1:2) were forced to be the same as for the polyanhydride in the second plateau (green). The same procedure was applied for the C 1s region, with the inclusion of two additional components at 289.5 eV (fwhm = 1.13 eV) and 285.4 eV (fwhm = 1.12 eV). The identical oxygen to carboxylic carbon ratios for both plateaus (3:2.0 for the first and 3:2.2 for the second) further support this. The carboxylic carbon to benzene carbon ratio for both plateaus (2:6.4 for the first and 2:6.3 for the second) also remains essentially identical to that of the intact phthalic acid (defined as 2:6), as expected for monomeric and polymeric phthalic anhydride.

The orientation of the anhydride species on the surface was investigated with near-edge X-ray absorption fine structure (NEXAFS), see Figure 5. At both 110 K, where the surface species is intact phthalic acid, and at 170 K, where both phthalic anhydride and polyanhydride coexist on the surface, the strong  $\pi^*$  absorption at grazing incidence and very weak absorption at normal incidence indicates that the molecules are oriented parallel to the surface. NEXAFS was measured for 110 and 170 K only.

A closer look at Figure 3 reveals two additional TPD features below room temperature, which we attribute to contamination, since we observe similar features for a clean Ag(100) sample



**Figure 5.** Carbon K-edge NEXAFS of 0.6 ML phthalic acid deposited on Ag(100) at 110 K (upper spectra) and 0.5 ML phthalic acid deposited at 170 K (lower spectra). Grazing and normal incidence spectra were measured at 80° incidence/20° emission and 0° incidence/60° emission relative to the surface normal, respectively. At 170 K, phthalic acid has completely reacted to form the anhydrides. Both the low temperature and 170 K species adsorb on the surface in a flat-lying geometry.

(not shown). The peak for  $m/z = 44$  at 150 K is assigned to  $\text{CO}_2$ -degassing from the Mo-heating wires. The  $m/z = 78$  peaks at 220 K for phthalic acid and 250 K for phthalic anhydride are close to the desorption peak of pure benzene from Ag(111) at  $\sim 205$  K.<sup>17</sup> We therefore attribute this feature to the coadsorption of benzene from the residual gas of the vacuum chamber, most likely originating from the phthalic acid/anhydride evaporator.

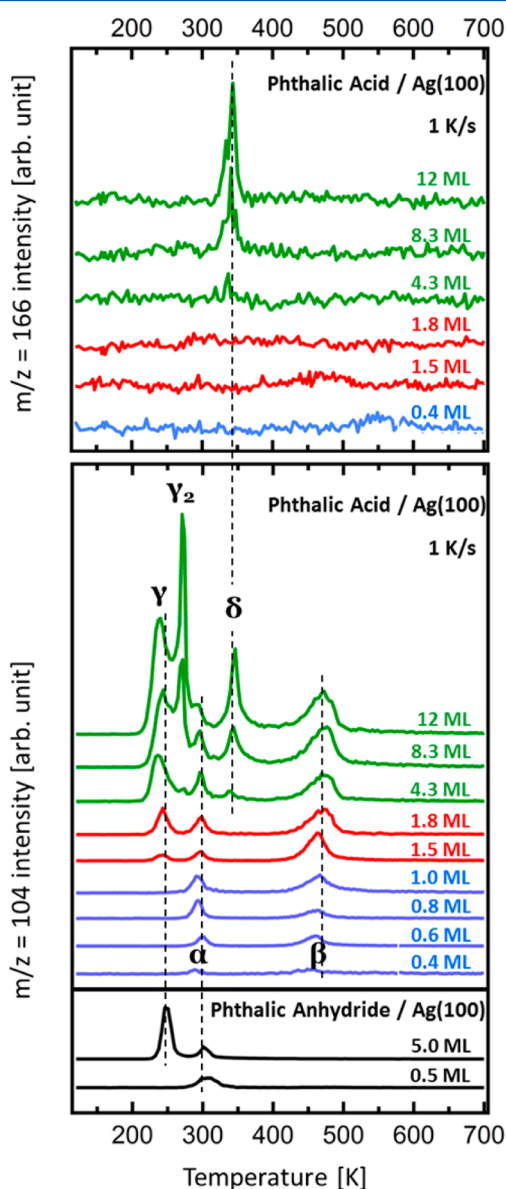
The third, stable plateau in the SR-XPS spectra in Figure 1 is observed from 400–450 K, which corresponds to the temperature range above 495 K in the TPD spectra in Figure 3. The O 1s region now consists of just one single narrow peak at 530.6 eV (fwhm = 1.26 eV, orange color), suggesting a single species rather than a convolution of two. Hence, all oxygen atoms are now equivalent, which is consistent with the formation of a bidentate carboxylate species ( $\text{COO}^-$ ). This species is also in agreement with the measured oxygen to carboxylic carbon ratio of 2:1.3. In addition, the carboxylic carbon to benzene carbon ratio of 2:6.3 for the polyanhydride decreases to 1:6.3, indicating only one carboxylate group per benzene ring. Simultaneously, the carbon coverage decreases from 0.3 ML (for the polyanhydride) to 0.1 ML, indicating a significant loss of carbon. Anhydride bonds that are cleaved upon heating to form carboxylates were also observed in a previous study investigating phthalic anhydride on Cu(110).<sup>18</sup> Carboxylate formation has, furthermore, also been suggested both for the adsorption of terephthalic acid on Cu(100)<sup>4</sup> and for the reaction of trimesic acid with Cu adatoms on Ag(111),<sup>6</sup> and the binding energy shifts observed there agree well with those we observe.

The loss of carbon is reflected in the TPD spectra in Figure 3 as desorption of phthalic anhydride ( $m/z = 104$ ) at  $\sim 450$  K (black curve). As expected for a decomposition product of polyanhydride, this TPD peak is not present when only phthalic anhydride is dosed on the surface (blue curve). The simultaneous desorption of water explains the reduced oxygen-to-carbon ratio. The carboxylate could be an upright standing species, as previously observed for different carboxylates on

copper surfaces<sup>19,20</sup> (sketched in Figure 4), or a flat lying species with silver adatoms linking the carboxylate groups together, similarly to what has been observed for other systems.<sup>10,19</sup>

As the surface is heated above 450 K, see Figure 1, first oxygen and then carbon disappears from the surface. While the oxygen signal vanishes completely, a very small amount of carbon (0.02 ML) remains on the surface even at 600 K. These observations are in line with the TPD spectra in Figure 3, which show desorption of CO<sub>2</sub> ( $m/z = 44$ ) and benzene ( $m/z = 78$ ) above 500 K. As the amount of carbon remaining on the surface is much lower than expected considering the hydrogen balance of the mentioned reactions, we suggest that the remaining carbon is lost by diffusion into the bulk of the Ag(100) crystal.

We have furthermore investigated the desorption behavior of multilayers of phthalic acid on Ag(100). In Figure 6 (bottom),



**Figure 6.** TPD spectra of  $m/z = 104$  (phthalic anhydride) from submonolayers and multilayers of phthalic acid on Ag(100) at a heating rate of 1 K/s. The lower two spectra show the corresponding desorption from a surface covered with phthalic anhydride.

desorption of phthalic anhydride ( $m/z = 104$ ) is shown for phthalic acid coverages up to 12 ML. At coverages below 1 ML (blue), we see two peaks, at  $\sim 300$  and 450 K (labeled in Figure 6 as  $\alpha$  and  $\beta$  peak, respectively), corresponding to phthalic anhydride monolayers and the decomposition of the poly-anhydride. As the coverage is increased above 1 ML, a third peak,  $\gamma$ , appears at 250 K at the position of phthalic anhydride multilayers,<sup>12</sup> indicating that the decomposition of phthalic acid to phthalic anhydride occurs even in the first several multilayers, which are still in the vicinity of the Ag(100) substrate. As the coverage is increased further, two more peaks appear at 270 ( $\gamma_2$ ) and 350 K ( $\delta$ ). We attribute the  $\gamma_2$  peak to desorption of crystalline phthalic anhydride multilayers, as opposed to desorption of more unstable amorphous multilayers at 250 K ( $\gamma$  peak). As the sample is heated up, there is competition between desorption from the metastable phase, giving rise to the  $\gamma$ -peak, and a phase transformation into the more stable phase which desorbs, forming the  $\gamma_2$  peak. Such phase transformations have been observed for, e.g., benzene,<sup>21</sup> several small organic molecules,<sup>22–24</sup> and recently also for phthalic anhydride.<sup>25</sup> The  $\delta$ -peak at 350 K is accompanied by peaks for phthalic acid ( $m/z = 166$ ), see Figure 6 (top), and water ( $m/z = 18$ ), see Figure 2, not present at lower coverages. We therefore conclude that the  $\delta$ -peak must originate from the desorption of phthalic acid multilayers, which are detected mostly as phthalic anhydride and water, because of decomposition of the acid on the walls of the Feulner Cup, before the molecules can be detected by the mass spectrometer.

## CONCLUSIONS

We have identified the temperature-dependent reactions of phthalic acid on Ag(100), as summarized in Figure 4. Phthalic acid adsorbs intact at 110 K, but decomposes to phthalic anhydride and polyanhydride at 150 K. When heated further, phthalic anhydride desorbs at 250 K, leaving only polyanhydride on the surface, which decomposes at 350 K into a carboxylate, through desorption of phthalic anhydride and water. The carboxylate is stable until 500 K, after which it decomposes, leading to desorption of CO<sub>2</sub> and benzene, and surface carbon, which mostly diffuses into the bulk, leaving only a little carbon on the Ag(100) surface at 600 K.

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### Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

XPS, X-ray photoelectron spectroscopy; SR, synchrotron radiation; TPD, temperature-programmed desorption; NEX-AFS, near-edge X-ray absorption fine structure

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