

# Sequential Bond Rearrangement of Unsaturated C<sub>3</sub>H<sub>3</sub> Groups Adsorbed on Ag(111)

*The internal bond rearrangement of chemisorbed unsaturated C<sub>3</sub>H<sub>3</sub> groups on Ag(111) have been identified by temperature-dependent X-ray photoemission spectroscopy (XPS), reflection absorption infrared spectroscopy (RAIRS) and density functional theory (DFT) calculations. The shift of 3d core-level binding energy (BE) of bromine and RAIR spectra taken after annealing a propargyl bromide (C<sub>3</sub>H<sub>3</sub>Br) covered Ag(111) surface to 200 K indicate the rupture of the C-Br bond and formation of an isomeric allenyl C<sub>3</sub>H<sub>3</sub> formalism, rather than propargyl. Sequential tautomerization of this allenyl into the third isomeric methylacetylide presentation was found to occur at 300 K, validated by C1s XPS and RAIR measurements. Theoretical cluster calculations assisted in the assignments of the characteristic vibrational bands involving the key surface intermediates to confirm the proposed sequential bond transformation processes.*

A diverse array of unsaturated C<sub>1</sub> (methylene and methylidyne) and C<sub>2</sub> (vinyl, vinylidene, ethylidene, and ethylidyne) bound to metal center(s) and surfaces has received much attention. In sharp contrast to the effort devoted to C<sub>1</sub> and C<sub>2</sub> ligands, complexes or surface bearing C<sub>3</sub> fragments have been less explored, especially the M-C<sub>3</sub>H<sub>3</sub> system, which include propargyl (M-CH<sub>2</sub>C≡CH), allenyl (M-CH=C=CH<sub>2</sub>), and acetylide (M-C≡CCH<sub>3</sub>) forms. To understand the bonding and reactivity of these C<sub>3</sub> species appended to an extended metal structure, propargyl bromide (Br-CH<sub>2</sub>C≡CH) was utilized as a precursor to generate C<sub>3</sub>H<sub>3</sub> fragments on a Ag(111) surface under ultra high vacuum conditions.

By exposing Ag(111) to 2 Langmuirs (L, 1 L=10<sup>-6</sup> Torr·s) propargyl bromide (commercially available from TCI, >97% purity) at 110 K, resulting in a fraction of a monolayer coverage, a series of temperature-dependent Br 3d X-ray photoemission spectra (XPS) is shown in Fig. 1. The broad curve (a) at 110 K can be systematically decomposed into two sets of 3d<sub>3/2</sub>/3d<sub>5/2</sub> spin-orbit splitting peaks, one at binding energy (BE) 70.6/69.8 eV and the other at 69.2/68.2 eV. The former doublet peaks are assigned to the C-Br BEs and the latter to Br bound directly to Ag. In agreement with previous work regarding CH<sub>3</sub>Br photodissociation on Ag(111) by Zhou and White,<sup>1</sup> we take the higher BE features as adsorbed molecules with C-Br bond intact and the lower BE state as species with C-Br bond cleaved. Therefore, propargyl bromide must adsorb both molecularly and dissociatively at this temperature. Annealing to 200 K, curve (b), leads to only one set of doublet peaks at 69.2/68.2 eV, indicating complete C-Br bond cleavage and generation of C<sub>3</sub>H<sub>3</sub> fragments on the surface. Further annealing to 240 K and higher temperatures, curve (c)-(f), produces no core-level shift, except that the peak areas start to decrease above 600 K. There is no detectable Br XP signal after heating to 900 K.

## ☉ Beamline

24A1 BM-(WR-SGM) XPS, UPS

## ☉ Authors

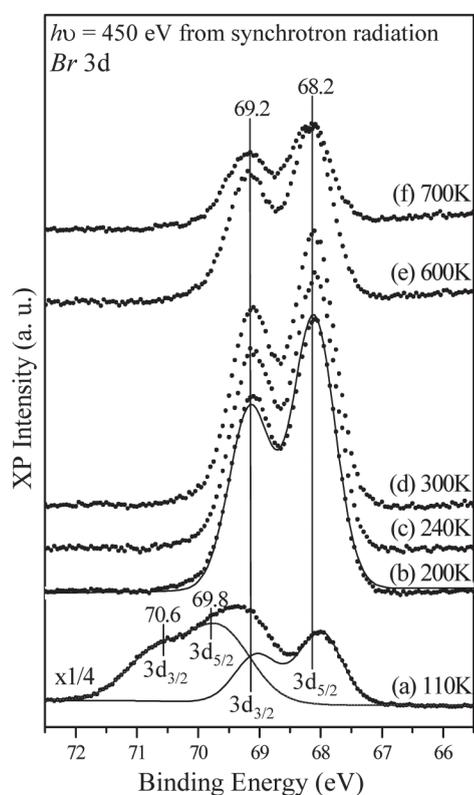
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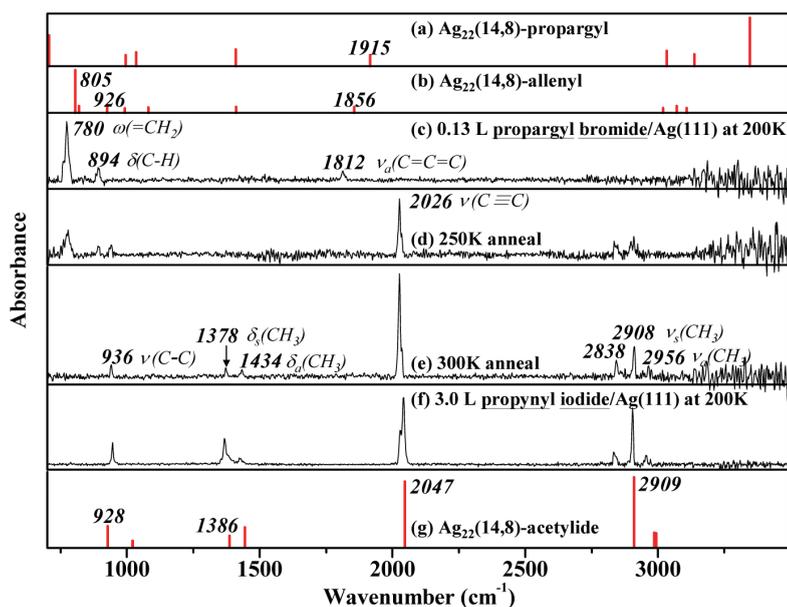
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**Fig. 1:** Variations of Br 3d XPS of propargyl bromide on Ag(111) with annealing temperature (Langmuir **18**, 1449, (2002))

Temperature-dependent RAIRS measurements were conducted to study the thermal transformation of the resulting organic  $C_3H_3$  moieties. Figure 2(c)-(e) show the temperature-dependent RAIR spectra for the Ag(111) exposed to 0.13 L propargyl bromide at 100 K, followed by heating of the surface to several key temperatures. All the spectra were measured at 100 K. In the 200 K IR spectrum, Fig. 2(c), three observable bands, 780, 894, and 1812  $cm^{-1}$ , were utilized to argue for a Ag- $\eta^1$ -allenyl formalism. To be certain, DFT calculations were launched with propargyl and allenyl units bound to a two-layer  $Ag_{22}(14,8)$  clusters and the computed IR frequencies are displayed in Fig. 2(a) and 2(b), respectively. Clearly those peaks in Fig. 2(b) appear to agree more reasonably with the experimental absorption bands in Fig. 2(c). The band at 1812  $cm^{-1}$  thus correlates with the asymmetric C=C=C stretch. The features at 894 and 780  $cm^{-1}$  represent the  $\alpha$ -C-H bending  $\delta$  (C-H) and terminal  $CH_2$  wagging  $\omega$ (=CH<sub>2</sub>) modes. After momentary annealing to 250 K, a number of new bands emerge from 936, 2026, 2838, and 2908  $cm^{-1}$  in Fig. 2(d); however, two of the signals diagnostic of  $\eta^1$ -allenyl (780 and 894  $cm^{-1}$ ) still persist. This spectral development suggests that allenyl begins to transform upon heating to generate an equilibrium mixture of  $\eta^1$ -

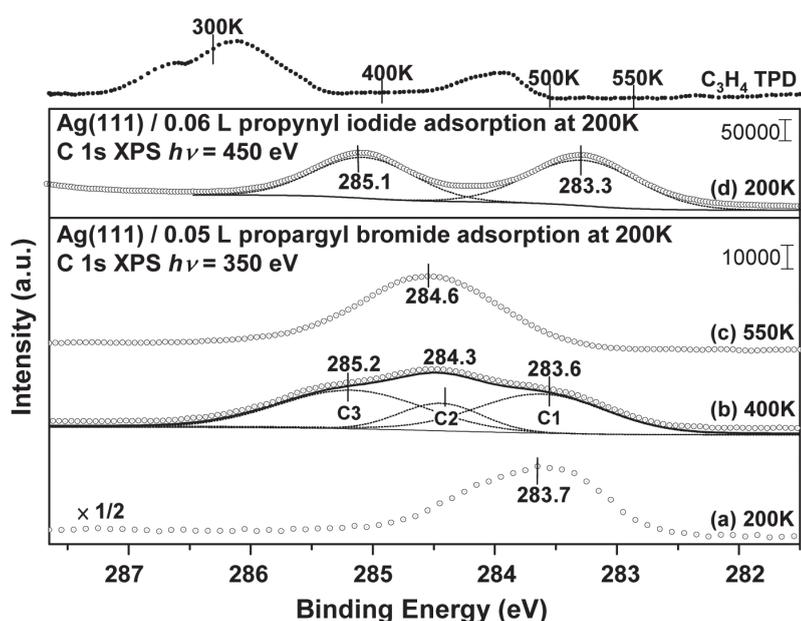


**Fig. 2:** Temperature-dependent infrared spectra of propargyl bromide ( $Br-CH_2-C\equiv CH$ ) and propynyl iodide ( $I-C\equiv C-CH_3$ ), in conjunction with the computed spectra of  $Ag_{22}(14,8)-CH_2-C\equiv CH$ ,  $Ag_{22}(14,8)-CH=C=CH_2$ , and  $Ag_{22}(14,8)-C\equiv C-CH_3$  by DFT calculations. (J. Am. Chem. Soc. **130**, 10263, (2008))

allenyl and a new surface species. The 300 K annealing ultimately makes the 780 and 894  $\text{cm}^{-1}$  bands disappear; instead, two more new band (1378 and 1434  $\text{cm}^{-1}$ ) arise as shown in Fig. 2(e). Intriguingly, it turns out that the six characteristic bands in Fig. 2(e) match remarkably well with those in the spectrum of Fig. 2(f), obtained by exposing Ag(111) to 3.0L of I-C $\equiv$ C-CH $_3$  (a direct precursor to the methylacetylide form, Ag-C $\equiv$ C-CH $_3$ ) at 200 K. The theoretical IR spectrum, built upon the optimized structure for methylacetylide bonded to the Ag $_{22}$ (14,8) cluster by DFT calculations are also displayed in Fig. 2(g). On the basis of the animated normal vibrations in the theoretical modeling, those peaks in the experimental Fig. 2(f) at 2956, 2908, 2026, 1434, 1378, and 936  $\text{cm}^{-1}$ , could be reasonably assigned to  $\nu_a(\text{CH}_3)$ ,  $\nu_s(\text{CH}_3)$ ,  $\nu(\text{C}\equiv\text{C})$ ,  $\delta_a(\text{CH}_3)$ ,  $\delta_s(\text{CH}_3)$ , and  $\nu(\text{C}-\text{C})$  modes, respectively. The information gathered above indicate that after C-Br bond scission, propargyl immediately converts into allenyl at 200 K, followed by the second isomerization into methylacetylide at 300 K.

The allenyl-methylacetylide conversion, in lieu of allenyl-propargyl tautomerization, is corroborated by XPS taken in a separate UHV chamber at the synchrotron facilities. The reported exposures for the XPS data were

set at the product saturation coverages calibrated by TPD conducted in that vacuum system. In Fig. 3(a), the C1s photoemission spectrum following adsorption of propargyl bromide on Ag(111) at 200 K exhibits a broad and asymmetric feature peaked at BE 283.7 eV with a full width at half-maximum (fwhm) of 1.27 eV. Here, no attempt was made to resolve the three different chemical environments of the carbon atoms in C $_3\text{H}_3$  because neither the chemisorbed nor gas-phase literature BE values for the allenyl species are available. After the surface was annealed to 400 K where the self-hydrogenation products (allene and propyne) are liberated as shown in the C $_3\text{H}_4$  TPD at the top of Fig. 3, the C1s spectrum shows notable changes in Fig. 3(b). First, the overall feature becomes extremely wide and shifts toward higher BEs. Deconvolution analysis, in which Shirley baseline is applied and line shapes are fitted with 100% Gaussian, reveals that this spectrum is best fitted with three components, shown as the dotted lines with peak maxima at 283.6 (C1), 284.3 (C2), and 285.2 eV (C3), respectively. Second, the integrated peak intensity is attenuated by about 28% with respect to Fig. 3(a). A previous XPS study of adsorbed methylacetylide formed by the reaction of propyne with



**Fig. 3:** (above) Temperature-programmed desorption of C $_3\text{H}_4$  and C 1s XP spectra of propargyl bromide and propynyl iodide. (J. Am. Chem. Soc. **130**, 10263, (2008))

$O_{(ad)}$  on Ag(110) showed only two C 1s peaks in a 5:3 ratio centered at 283.1 and 284.9 eV.<sup>2</sup> To be sure, separate XPS measurements of methylacetylide again by dissociatively adsorbed  $I-C\equiv C-CH_3$  at 200 K on Ag(111) was carried out. The C1s spectrum, Fig. 3(d), also illustrates two peaks in a 5:4 ratio centered at 283.3 and 285.1 eV. The discrepancies might be due to the electronic effects originating from the utilization of halide compounds as the  $C_3H_{3(ad)}$  in our case. Yet the comparable BE information of Fig. 3(d) ensures assignments of the C1 and C3 peaks to methylacetylides in Fig. 3(b). The remaining peak at 284.3 eV can be carbon bonded to hydrogen ( $CH_x$ ), confirming that the surface may be partially covered with a carbonaceous (or hydrocarbonaceous) overlayer. It is quite possible that hydrogen transfer to the  $C_3H_{3(ad)}$  may be mediated by this type of active carbon deposits, rather than via direct addition of adsorbed hydrogen atoms on the bare silver sites (Ag has low affinity for hydrogen). Finally, when the surface containing methylacetylide is heated to 550 K, only a single C1s peak with BE at 284.6 eV (graphitic) is observed in Fig. 3(c).

When information are taken together, we conclude that propargyl bromide undergoes C-Br bond scission concomitant with a [1,3]-sigmatropic rearrangement to form allenyl at 200 K on Ag(111). Further heating to 300 K, the allenyl form is reorganized again via [1,3]-hydrogen shift to render the methylacetylide species, demonstrating an unprecedented triple migration from the terminal to the internal position inside a MCCC framework. ◆

### Experimental Station

Surface-interface end station

### Publications

1. Y. -J. Wu, W. -H. Wang, and C. -M. Chiang, *Langmuir* **18**, 1449-1452 (2002).
2. H. Kung, S. -M. Wu, Y. -J. Wu, Y. -W. Yang, and C. -M. Chiang, *J. Am. Chem. Soc.* **130**, 10263-10273 (2008).

### References

1. X. -L. Zhou and J. M. White, *Surf. Sci.* **241**, 259 (1991).
2. J. M. Vohs, B. A. Carney, and M. A. Barteau, *J. Am. Chem. Soc.* **107**, 7841 (1985).

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