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Observation of *β*-C−H Bond Activation of Allyl Groups Adsorbed on Ag(111) and an Unusual Deuterium Isotope Effect

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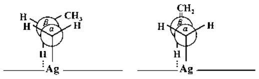
Surface *allyl* has been recognized as a key intermediate in a new catalytic cycle proposed for Fischer−Tropsch synthesis.[1] This so-called *alkenyl* mechanism reveals that the polymerization process is initiated by the insertion of methylene into the metal−*vinyl* (sp^2 carbon) bond to give a surface *allyl* (sp^3 carbon). The *allyl* then isomerizes to a *propenyl* (sp^2 carbon), which in turn can combine with more methylenes to extend the carbon chain length sequentially. Due to our previous success in mimicking the methylene insertion into the metal−*alkyl* bond under ultrahigh-vacuum conditions on a silver surface,[2,3] we undertook an investigation concerning the reactivity of *allyl* groups chemisorbed on atomically clean Ag(111). We did not obtain any evidence for the allyl/propenyl isomerization ($Ag{-}C^{\alpha}H_2{-}C^{\beta}H{=}C^{\gamma}H_2$/$Ag{-}CH{=}CH{-}CH_3$); however, we discovered that the *β*-C−H bond in the allyl moiety can be activated (*β*-hydride elimination) to afford *allene* ($CH_2{=}C{=}CH_2$). This is a somewhat surprising result because although *β*-H elimination is the most well documented fundamental step for *β*-hydrogen-containing *alkyls* on many surfaces,[4,5] this step is *not favored* at all on *silver* due to its low affinity for hydrogen.[4] Rather, the C−C bond-forming reactions prevail. There is ample precedent[6] which showed that methyl, ethyl, *n*-propyl, and isopropyl groups on Ag(111) dimerize to yield ethane, butane, *n*-hexane, and 2,3-dimethylbutane, respectively, all with 100% selectivity. In fact, Carter and Anton[7] have reported that the chemisorption of allyl chloride on Ag(110) can lead to a *π*-bonded allylic moiety with subsequent formation of 1,5-hexadiene (diallyl), which is also a result of C−C self-coupling. Nevertheless, we believe that allyl's *β*-H elimination pathway might have been overlooked previously, and its accessibility compared to that of silver alkyls can be justified by deliberating on their transition-state (TS) energetics.

Consensus about *β*-hydride elimination processes is that this type of reaction involves a *cyclic* TS (syn elimination), a geometry where two carbon atoms (the α- and *β*-carbons), one hydrogen atom (*β*-hydrogen), and the surface metal atom(s) are coplanar.[8−10] When this requirement is imposed on a surface *allyl* group, a *σ*-bound metal−allyl species must be invoked. Posing a surface *propyl* as contrast, we can visualize and compare their TS configurations in Scheme 1. The Newman projections serve to reveal the relative positions of the hydrogen atoms and substituents on the α- and *β*-carbons. In the allyl TS (right), the methylene group (viewed as a substituent) on the back carbon is *staggered* with respect to the two hydrogen atoms on the front carbon. In the propyl TS (left), the methyl group and the hydrogen atom on the back carbon are in an *eclipsed* conformation relative to the two hydrogen atoms on the front carbon. Hence, the total destabilization of the TS resulting from steric repulsion in allyl is not as severe as that in the propyl counterpart, making the *β*-C−H bond activation for allyl groups less energy intensive.

Scheme 1



We set out to verify the *β*-hydride elimination pathway from allyl iodide chemisorbed on Ag(111) utilizing temperature-programmed reaction/desorption (TPR/D) spectrometry (experiments were performed in an ultrahigh-vacuum chamber described in detail elsewhere[3]). Allyl halides (C_3H_5X, X = Cl, Br, I) can lead to the desired $C_3H_{5(ad)}$ on a variety of metal surfaces[7,11−13] by breaking the weak C−X bond upon adsorption, even at cryogenic temperatures. To ensure empty-site availability for a desired bond-dissociating step (*β*-H elimination) and to discourage a bimolecular bond-making reaction (allyl dimerization), we focus on the low-coverage results. After exposing Ag(111) to 0.05 L (1 L = 10^{-6} Torr·s) allyl iodide at 200 K (no physisorbed multilayer), TPR/D did not observe any intact molecule desorbing (*m*/*e* 168), but, instead, iodine atoms (*m*/*e* 127) were found to evolve from the surface above 700 K, suggesting that all the adsorbed C_3H_5I undergoes C−I bond scission. A multiple-ion survey in conjunction with detailed cracking pattern analysis can uncover the identities of the volatile hydrocarbon products, displayed in Figure 1 (left). Here, the *m*/*e* 67 ($C_5H_7^+$) feature at 280 K represents the expected C−C coupling product, 1,5-hexadiene (parent ion $C_6H_{10}^+$ is not pronounced, with 70 eV ionization energy in the mass spectrometer[14]). However, the relative abundance (based on the integrated peak areas) of *m*/*e* 67, 42, 41, 39, 38, and 37 signature fragments, reported as "total" in Table 1, does not match the cracking pattern of 1,5-hexadiene. Specifically, fragments of *m*/*e* 42, 38, and 37 are supposed to be negligible, and *m*/*e* 39 and 41 seem too large relative to *m*/*e* 67, implying that there are contributions from other hydrocarbon compounds. We notice that the ratio from the quite significant signals of *m*/*e* 37 and 38 nearly duplicates that of pure *allene* (see Table 1, *m*/*e* 37:38 = 0.7 ± 0.1 (TPR/D) vs 0.76 ± 0.04); the peak temperature (295 K) actually deviates from the 6C product (280 K). *The formation of allene* ($C_3H_{5(ad)} \rightarrow C_3H_{4(g)} + H_{(ad)}$) *provides good evidence for the β-hydride elimination step.* Further, this elimination reaction occurs at only a 15 K higher temperature than allyl dimerization ($C_3H_{5(ad)} + C_3H_{5(ad)} \rightarrow C_6H_{10(g)}$), indicating that unlike the case with alkyls, the C−C bond-forming step of allyl groups does not 100% dominate. When the intensity contribution of *m*/*e* 39 from allene is subtracted (see "total − A" in Table 1), followed by another deduction of the *m*/*e* 39 and 41 contributions from 1,5-hexadiene (see "total − A − H"), the net 39:41:42 turns out to match the fragmentation ratios of propene (0.6:1:0.7). The production of propene is attributed to the hydrogen atoms, resulting from the *β*-elimination, scavenged by the residual allyl groups on the surface ($C_3H_{5(ad)} + H_{(ad)} \rightarrow C_3H_{6(g)}$).

To substantiate the *β*-H elimination step, a *β*-deuterium-labeled allyl iodide ($IC^{\alpha}H_2{-}C^{\beta}D{=}C^{\gamma}H_2$) was synthesized on the basis

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Table 1. Relative Peak Intensities for Both the Mass Spectra of Pure Allene, 1,5-Hexadiene, and Propene and Multiplex TPR/D Traces from Allyl Iodide Adsorbed on Ag(111)

selected ions, *m*/*e*	mass fragmentation ratios[a]			TPR/D data		
	allene	1,5-hexadiene	propene	total[b]	total − A	total − A − H
37	0.76 ± 0.04			15.5 ± 1.6 (0.7 ± 0.1)		
38	1			21.7 ± 2.1 (1)		
39	2.17 ± 0.08	0.53 ± 0.03	0.62 ± 0.01	100	52.9 ± 4.9	24.3 ± 5.9 (0.6 ± 0.2)
41		0.91 ± 0.05	1	91.9 ± 4.8	91.9 ± 4.8	42.9 ± 6.8 (1)
42			0.70 ± 0.01	32.0 ± 4.5	32.0 ± 4.5	32.0 ± 4.5 (0.7 ± 0.2)
67		1		53.9 ± 5.2	53.9 ± 5.2	

[a] See ref 14 (only significant ion fragments are listed). [b] A blank multiplex TPR/D was first measured as the background, which we subtracted from the TPR/D signals after adsorbing allyl iodide, and then the raw integrated peak areas of *m*/*e* 37, 38, 41, 42, and 67 were normalized to the largest 39 amu signal (as 100). Ten sets of multiplex TPR/D traces similar to those in Figure 1 (left) were used to determine the averages and errors.

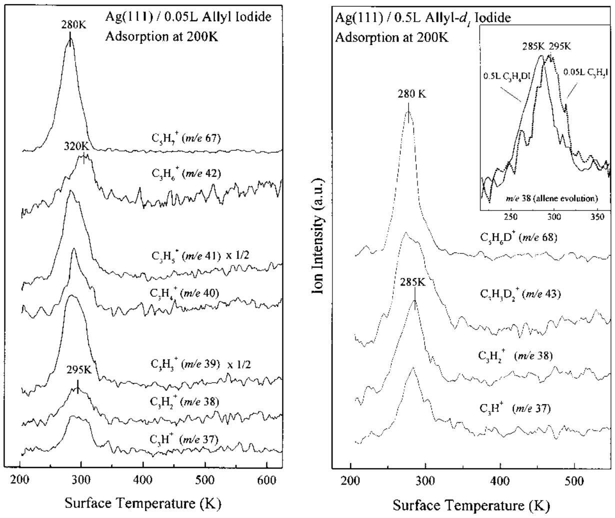
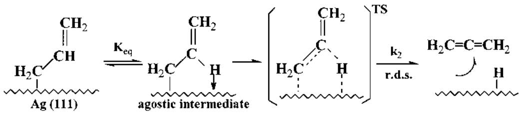


Figure 1. (Left) Multiple-ion TPR/D spectra after the adsorption of 0.05 L C_3H_5I on Ag(111) at 200 K. Note that *m*/*e* 39 and 41 signals are reduced by half. Ions were monitored with the mass spectrometer ionizer energy set at 70 eV. The heating rate was 2 K/s. (Right) Multiplex TPR/D traces after the adsorption of 0.5 L C_3H_4DI on Ag(111) at 200 K. Inset: The *m*/*e* 38 signal from the left panel, representing *allene* evolution due to β-hydride elimination of C_3H_5I, is overlapped with the signal from C_3H_4-DI to exhibit the kinetic isotope effect.

of the procedure by Landauer and Rydon.[15,16] The purity of the compound and the position of the deuterium atom were confirmed by GC−MS, in situ mass spectrometry, and ^{1}H NMR, respectively. Multiplex TPR/D traces after the adsorption of 0.5 L[17] allyl-d_1 iodide are shown in Figure 1 (right). The *m*/*e* 68 signal indicates the evolution of deuterated diallyl from self-coupling. Normal allene, following the β-D elimination, is again characterized by the pronounced features at *m*/*e* 37 and 38. The emergence of *m*/*e* 43 ($C_3H_3D_2^+$, a fragment ion of propene-d_2) affirms the incorporation of the deuterium atom (from the elimination step) into the allyl-d_1 group. Since TPR/D spectra can be used to evaluate the activation energy for the reaction/desorption kinetics of molecules from the surfaces,[18] the deuterium isotope effect was measured as an indicator for the β-C−H(D) bond activation process. In the inset of Figure 1 (right), we overlap the two allene TPR/D peaks together. Intriguingly, the peak from allyl-d_1 seems to shift toward *lower* temperatures. The magnitude of the kinetic isotope effect can be estimated by using their peak temperatures (295 K (β-H) vs 285 K (β-D)) and Redhead's analysis.[19] We obtain a deuterium isotope effect of $k_{obs}^D/k_{obs}^H = 3.3 \pm 0.5$ (the statistical uncertainty was based on three experiments) at 300 K, which indicates $k_{obs}^H < k_{obs}^D$, an *inverse isotope effect*. This inverse effect seems unusual for surface reactions; however, it is not unprecedented in the organometallic literature. Bergman et al.[20] observed a large inverse isotope effect for C−H bond activation of cyclohexane-d_0 and -d_{12} by Cp*Rh(CO)$_2$. A rationale was provided in Bergman's study: that is, a measured "kinetic" isotope effect (KIE) for an overall reaction often simply reflects an "equilibrium" isotope effect (EIE) of steps prior to the rate-determining step (rds). Adopting this concept, we propose the following mechanism (see Scheme 2) to interpret the observed inverse KIE for β-elimination of allyl groups. Here we postulate that the adsorbed allylic moiety quickly achieves equilibrium with a surface-bound *agostic* intermediate,[21] in which the surface Ag atoms interact with the β-hydrogen (deuterium), but the β-C−H(D) bond has not yet been activated. Since the Ag−D bond is substantially stronger than the Ag−H bond (54.2 versus 51.4 kcal/mol),[22] a large inverse EIE ($K_{eq}^H/K_{eq}^D \ll 1$) is expected due to such enthalpic nature. Even though we might predict a normal KIE for the β-C−H(D) bond cleavage step ($k_2^H/k_2^D > 1$) simply considering the zero-point energy (ZPE) difference associated with the C−H and C−D stretching frequencies along the reaction coordinate,[23] the combined effect on the apparent rate constant $k_{obs} = K_{eq}k_2$ is still inverse ($k_{obs}^H/k_{obs}^D < 1$).

Scheme 2



In conclusion, TPR/D in conjunction with deuterium labeling has clearly demonstrated that chemisorbed allyl on Ag(111) can be transformed into allene, providing the first example for the β-C−H bond activation on a single-crystal silver surface. The rich assortment of chemistry on Ag surfaces is made possible with allyl groups as opposed to alkyls, and the notion that the reactivity of silver surfaces is limited to C−C bond-forming reactions should be modified.

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