

Photochemistry of Vinyl Chloride Physisorbed on Ag(111) through Molecular Anion Formation Induced by Substrate Electron Attachment

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Pulsed 266 and 355 nm ultraviolet laser irradiation of monolayer vinyl chloride physisorbed on Ag(111) results in molecular dissociation leading to C_2H_3 and Cl, much of which is adsorbed to the surface. On the basis of observations made on dissociation dependences on chlorine isotope and photon energy, it is deduced that upon excitation vinyl chloride forms a transient negative ion through a substrate mediated, vertical electron attachment mechanism. The anion either dissociates or relaxes through energy transfer to the neutral state causing the neutral molecule to desorb. The threshold for vertical attachment of substrate electron is estimated to be 0.8 eV below the vacuum level, in agreement with the experimentally observed wavelength dependence in photoinduced dissociation. Chemisorbed Cl on the Ag(111) surface inhibits the photodissociation process by increasing the substrate work function and consequently the energy threshold for electron vertical attachment. Upon heating the Ag(111) surface, adsorbed vinyl combines to produce 1,3-butadiene in a first order, diffusion limited, process with an activation energy of 10.4 kcal/mol.

I. Introduction

One motivation for studying photochemistry of molecules adsorbed on metals is to examine to what extent the presence of the substrate affects the properties of the adsorbed molecules. Because of the weak interaction with the surface for physisorbed molecules, it is anticipated that the adsorbate is relatively unperturbed and retains many of the properties of its gas-phase counterpart. On the other hand, previous studies on the photochemistry of molecules such as formaldehyde have shown that because of the rapid relaxation of excitation energy in the molecule, photochemistry is induced through a dissociative negative ion state accessed through substrate mediated molecular excitation, which results from photon absorption by the metal.^{1,2} Furthermore, the dominant dissociation channel is very different from the gas-phase dissociation channel because of the adsorbate–substrate interactions.^{3–5}

In general, photon induced surface chemistry of adsorbates on metal surfaces is governed by two excitation mechanisms: direct photon absorption by the adsorbate or via substrate mediated molecular excitation resulting from photon absorption by the metal.^{6–8} Since vinyl chloride physisorbs on Ag(111) virtually unperturbed,⁹ by selecting photons in an energy regime where gas-phase vinyl chloride does not absorb, one expects that any photochemistry that may occur arises from the substrate mediated mechanism. Vinyl chloride is a molecule for which previous gas-phase spectroscopic studies have indicated the presence of a negative ion state.^{10–14} This negative ion state in the energy region accessible through photoexcited substrate electrons suggests possible photochemical activity through the substrate mediated mechanism. As many prior photochemical studies of organic molecules on metal, some referred to later in this report, were mostly on molecules chemisorbed on surface, the physisorbed vinyl chloride provides an interesting case for consideration. Previously, formaldehyde on Ag was perhaps the only other physisorbed system that has displayed substrate-

electron mediated photochemical activities.² Vinyl chloride adsorbed on metals offers additional interest for investigation because of its widespread use in industry. Would vinyl chloride dissociate at all upon light irradiation? Would the dissociation lead to vinyl and chlorine as well as HCl and acetylene as in the gas-phase reactions?¹⁵ Would the dissociation products adsorb on the surface? Would they further react, and even polymerize on the surface like formaldehyde on Ag?²²

We have characterized the adsorption state and thermally induced desorption/dissociation of vinyl chloride on Ag(111).⁹ Vinyl chloride physisorbs with little perturbation at temperatures below 119 K. The molecular plane is approximately parallel to the surface plane, with the molecular axis tilted $\sim 30^\circ$ off parallel. As the surface is heated, there is a competition between molecular desorption (peak at 119 K) and dissociation (starting at 126 K) with approximately 80% or more of the adsorbate desorbing molecularly. The first-order desorption for physisorbed molecular vinyl chloride has an E_a of 6.7 kcal/mol and prefactor of $4.6 \times 10^{11}/s$.⁹ At 126 K, a small portion ($<20\%$) dissociates into vinyl and Cl, which then recombine to form vinyl chloride at temperatures higher than 145 K (the recombination desorption peak temperature is coverage dependent) in a second-order process with an E_a of 10.7 kcal/mol and a second-order prefactor of $0.0023 \text{ cm}^2/(\text{molecule}\cdot s)$.⁹

Here we report observations made on light (266, 355, and 532 nm) induced dissociation and desorption of vinyl chloride on Ag(111). It is deduced that photon induced dissociation of physisorbed vinyl chloride is through a substrate mediated mechanism and that the photochemical behavior is strongly affected by the presence of the metal surface and the negative ion state of the molecule. This study once again highlights the importance of the existence of the dissociative negative ion state of the molecule in order to have apparent photochemistry in the soft UV light region while adsorbed on the metal surface.

II. Experimental Section

The experiments were conducted in a UHV chamber with a base pressure of 1×10^{-10} Torr. The chamber was used for

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thermal desorption spectroscopy (TDS) and photochemistry experiments. The Ag(111) sample with 1.5 cm diameter surface is mounted on a cryostat cooled with liquid nitrogen to a base temperature below 85 K and is cleaned with cycles of Ne sputter and anneal before vinyl chloride adsorption. Vinyl chloride (Matheson, 99.5% purity) is further purified by passing the gas through a series of two cyclohexane slush baths ($\sim 6^\circ\text{C}$) to remove inhibitors and impurities, then condensing it in liquid nitrogen cooled, sealed glass sample containers. Dosing of vinyl chloride on Ag(111) is through the backfilling method. TDS experiments with exposures from 0.20 to 10.0 Langmuir (L) are used to determine the coverage–exposure relationship and identify 4.0 L as the exposure beyond which monolayer (ML) saturation is reached. For the TDS experiments reported here, the crystal is resistively heated at 1 deg/s from the base temperature to 730 K. The sample is positioned with the surface normal pointing perpendicularly to the 0.385 cm diameter nose cone entrance of the mass spectrometer (UTI 100C), ensuring that the monitored species are from the sample surface rather than other chamber surfaces. The mass spectrometer had a channel electron multiplier detector and could detect species with mass-to-charge ratios of 1 to 150. The spectrometer used low light emitting thoriated iridium filaments to minimize complications for the photochemistry experiments. The photochemistry experiments were analyzed via TDS before and after irradiation. Details of the UHV and TDS setup can be found elsewhere.²

The photochemistry experiments are performed with pulsed laser light generated by a Nd:YAG laser (Continuum 661-20) operating with 20 Hz repetition rate. The 532, 355, or 266 nm output of the laser is expanded to a 2.0 cm diameter parallel beam with a Galilean telescope and passes through a 1.5 cm diameter iris immediately before entering the chamber through a CaF_2 window, so that the beam illuminates the entire 1.5 cm diameter crystal surface. The power is measured just before the beam enters the chamber with a calibrated, wavelength specific, volume absorber power meter (ScienTech). The beam impinges on the crystal at a 45° incidence angle. The 532 nm light is s-polarized. The 355 and 266 nm light is p-polarized. The light beam reflected from the crystal surface exits the chamber through a sapphire exit window located 90° from the entrance window to minimize stray light in the chamber.

The laser is operated at low pulse power with typical values of 0.5–5.0 mJ/pulse, depending on light wavelength. The nominal pulse length is 10–20 ns. The low light intensity is used to avoid bulk crystal heating. Indeed, no discernible crystal temperature increase was measured by the thermocouple mounted to the sample during photochemistry experiments. As an example, considering the typical photochemistry experiment using 266 nm light with 2 mJ/pulse maximum power and a laser pulse width of 14 ns, Ag reflectivity of 0.25 at 266 nm, and incident angle of 45° , less than 1.5 mJ is absorbed by the substrate. This absorbed energy distributed over the entire surface area of the substrate would cause a transient temperature rise of less than 5 K over a period of 10^{-7} s, as estimated by the classical heat conduction equation.^{17–19}

III. Results and Analysis

A. Post Irradiation TDS. The top panel in Figure 1 shows TDS curves of mass 62 ($\text{C}_2\text{H}_3^{35}\text{Cl}$) and mass 64 ($\text{C}_2\text{H}_3^{37}\text{Cl}$) for 0.50 ML vinyl chloride adsorbed on Ag(111). Upon adsorption at 87 K, vinyl chloride physisorbs on Ag(111) and retains its gas-phase molecular character.⁹ As the temperature is increased, TDS curves display the characteristic first-order desorption for

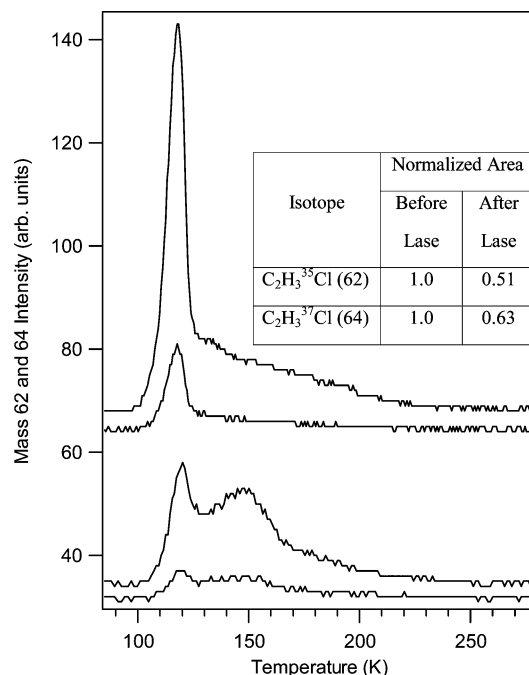


Figure 1. TDS for 0.50 ML vinyl chloride physisorbed on Ag(111) without (top) and with (bottom) 266 nm light irradiation (0.70 mJ/pulse, 20 Hz, for 20 min and a total fluence of 1.2×10^{19} photons/cm²). For each pair of curves, the top is mass 62 and the bottom is mass 64. The inset is the normalized integrated areas for mass 62 and 64.

physisorbed molecular vinyl chloride peaked at 119 K. At temperatures greater than 126 K, there is a competition between molecular desorption and thermally induced dissociation, as described in our previous study.⁹ Approximately 80% of the vinyl chloride molecules desorb while a small portion ($<20\%$) dissociate into vinyl and Cl, which then recombine at higher temperatures with a vinyl chloride desorption peak at 155 K in a second-order process.⁹ A detailed discussion and analysis of this 155 K peak, which is difficult to discern in the top panel of Figure 1 at this particular vinyl chloride coverage, can be found in ref 9, which clearly demonstrates the presence of the small, second-order recombinative desorption peak at this temperature.

The lower panel in Figure 1 shows TDS curves of the physisorbed vinyl chloride system following irradiation with 266 nm light. The curves again show the characteristic desorption signature for physisorbed molecular vinyl chloride as well as the recombinative desorption feature. There are, however, notable differences between the top and bottom pairs of curves. First, based on integrated areas under the TDS curves with and without irradiation, we note that a significant amount (30–50%) of the initially physisorbed vinyl chloride has desorbed during irradiation. The second observation is that the total integrated area under the mass 62 curve with irradiation is 51% of the area without irradiation, while the total integrated area under the mass 64 curve with irradiation is 63% of the area without irradiation. Third, the ratio of vinyl chloride in the physisorbed desorption feature to the recombinative desorption feature is lower for the TDS curves with irradiation as compared to the curves without irradiation.

The effect of coverage in photochemistry has been examined. Figure 2 shows TDS curves of 0.125 ML vinyl chloride with and without irradiation. As with Figure 1, the TDS in Figure 2 shows the first-order, physisorbed molecular desorption feature at 119 K and the coverage dependent, second-order recombi-

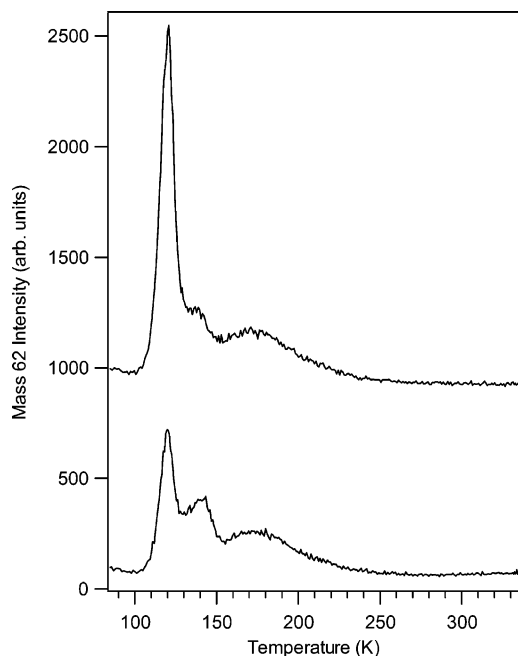


Figure 2. TDS for 0.125 ML vinyl chloride physisorbed on Ag(111) without (top) and with (bottom) 266 nm light irradiation (1.1 mJ/pulse, 20 Hz, for 10 min and a total fluence of 9.3×10^{18} photons/cm²).

native desorption feature at 180 K. Unlike Figure 1, though, the very low coverage enables the resolution of a new feature at 137 K in the upper panel of Figure 2 and at 142 K, with proportionally larger quantity, in the lower panel of post-irradiation TDS. The desorption curve for this new feature appears first order and with use of the Redhead approximation gives an E_a of 8.8 kcal/mol.²⁰ Note also that as in Figure 1, for Figure 2 the total integrated area with irradiation is less than that without irradiation and the ratio of desorbed vinyl chloride compared to recombinative desorption is lower with irradiation than without.

In addition to vinyl chloride desorbed from the surface, other photochemistry products have been searched for in post-irradiation TDS. We searched for desorbed species with masses from 2 to 100 amu over a temperature range of 85–650 K. Figure 3 shows TDS of mass 54 after irradiating 0.50 ML vinyl chloride with 266 nm light. The feature at 249 K is low in intensity and is the only other desorption feature found in these post-irradiation TDS. The 249 K feature is found also for masses 53, 52, and 39 and the overall fragmentation pattern of all these masses matches that in the literature²¹ for 1,3-butadiene, which is confirmed with the mass spectrum of 1,3-butadiene taken in our chamber.

The source of the 1,3-butadiene can be deduced by comparison with TDS of 1,3-butadiene dosed in our chamber at low coverage on Ag(111), which shows a broad feature in a first-order desorption process with a peak temperature of 166 K. A Redhead analysis²⁰ gives an approximate E_a of 10 kcal/mol for the molecular 1,3-butadiene desorption. This TDS peak shape is quite dissimilar to the sharp 249 K feature in the post-irradiation TDS of Figure 3. We therefore attribute the 249 K feature to surface C_2H_3 fragments combining to form 1,3-butadiene.

1,3-Butadiene arises as a secondary product in the TDS of photoirradiated vinyl chloride but not as a secondary product in thermally induced dissociation of vinyl chloride. After irradiation the following species are on the surface: residual molecular vinyl chloride, and vinyl and Cl which exist in unequal numbers with more vinyl than Cl since Cl can be ejected

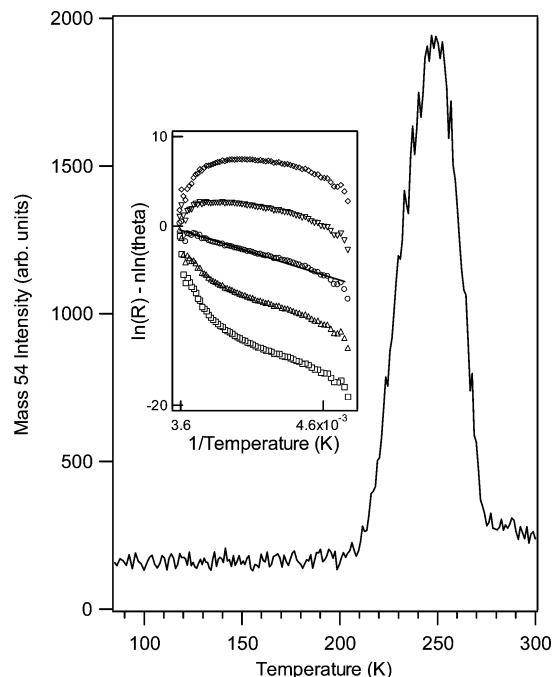


Figure 3. TDS of mass 54, identified as 1,3-butadiene, which is formed when C_2H_3 and C_2H_3 combine on the surface at 249 K. The C_2H_3 species are formed by irradiating 0.50 ML vinyl chloride physisorbed on Ag(111) with 266 nm light (1.8 mJ/pulse, 20 Hz, for 44 min and a total fluence of 7.2×10^{19} photons/cm²). The inset shows fitting of data for reaction order of 0, 1/2, 1, 3/4, and 2 (top to bottom).

from the surface during photoirradiation.²² As the surface is heated in post-irradiation TDS, 80% of the residual molecular vinyl chloride desorbs molecularly while 20% dissociates to vinyl and Cl. The surface adsorbed vinyl and Cl, formed from both thermal and photoinduced dissociation, then recombine in the second-order process resulting in the 155 K desorption feature. At temperatures greater than 155 K, the only remaining species adsorbed on surface is vinyl, which would then recombine to form 1,3-butadiene at 249 K. In the case of TDS of vinyl chloride adsorbed without any photoirradiation, thermal dissociation leads to an equal amount of vinyl and Cl on the surface. Two vinyls forming butadiene is not thermodynamically feasible at temperatures less than 249 K. At 155 K though, all vinyl and Cl recombine in pairs and there are no surface species remaining beyond 155 K. Therefore butadiene is not expected to result from vinyl recombination in TDS of vinyl chloride without photoirradiation.

The assignment of the 142 K feature, which is unresolved in higher coverage experiments (Figure 1) but appears in low coverage experiments (Figure 2), requires further consideration. We propose that this TDS feature is due to desorbing molecular vinyl chloride that is bound more tightly to the surface, due to the presence of Cl coadsorbed on the surface, than the physisorbed vinyl chloride on a clean surface. It is likely that the effect of the adsorbed Cl is due either to direct interaction of adsorbed vinyl chloride with Cl or indirect interaction through changes in the surface electronic structure due to Cl adsorption. Since vinyl chloride is physisorbed on Ag(111), we speculate that the effect is most likely through the Cl charge–vinyl chloride dipole interaction. Cl adsorbed on Ag(111) carries a partial negative charge due to its electron withdrawing effect. As a result, the charge-dipole attraction between Cl and vinyl chloride, with a molecular dipole of 1.4 D, would result in a higher vinyl chloride desorption temperature than on the surface without adsorbed Cl.

The coadsorbed Cl arises from two sources. The first source is from thermally induced dissociation of vinyl chloride. As previously noted, when the surface is heated from the base temperature during TDS, there is a competition between molecular desorption and thermally induced dissociation. As the surface temperature passes 126 K, a small quantity of molecular vinyl chloride dissociates to C_2H_3 and Cl. While the majority of the physisorbed vinyl chloride has desorbed molecularly by 126 K, the adsorption energy of the small quantity of molecularly adsorbed vinyl chloride remaining is increased due to interaction with the coadsorbed Cl. This more tightly bound vinyl chloride accounts for the 137 K shoulder in the top curve of Figure 2 for 0.125 ML without irradiation. Interestingly, our results show that in experiments without irradiation, all of the vinyl chloride that thermally dissociates at 126 K recombines and desorbs at higher temperature, leaving a clean Ag(111) surface, indicating a one-to-one correspondence between adsorbed Cl and vinyl during a TDS experiment without irradiation. This result is contrasted to the photochemistry experiments, where we postulate that irradiation causes some Cl to be ejected from the surface during the dissociation process, an observation reported in other photochemistry experiments with small chlorinated molecules on the Ag(111) surface²² but which cannot be confirmed in our experiments as the mass spectrometer was not configured for detecting the ejected Cl^- ion. The ejection of Cl leaves excess C_2H_3 remaining on the surface. This excess C_2H_3 subsequently recombines to form C_4H_6 at 249 K during TDS.

The second source of coadsorbed Cl is from photon-induced dissociation of vinyl chloride. As previously noted, the 249 K feature of Figure 3 is for 1,3-butadiene, which only occurs after irradiation. The 1,3-butadiene is most logically from the combination of two C_2H_3 molecules resulting from dissociation of vinyl chloride into C_2H_3 and Cl. The post-irradiation TDS shown in the bottom panel of Figure 2, then, has a significantly larger peak at 142 K, which corresponds to the larger quantity of vinyl chloride adsorbed in the vicinity of coadsorbed Cl. We have tested this interpretation by preadsorbing Cl on the Ag(111) surface, then dosing vinyl chloride and conducting TDS without irradiation. The TDS with preadsorbed Cl and without irradiation has a molecular vinyl chloride desorption feature at about 142 K, and depending on the amount of preadsorbed Cl, it mirrors the post-irradiation TDS feature at 142 K shown in Figure 2.

In summary, there are four TDS features described above and as shown in Figures 1–3, which result after irradiation of vinyl chloride/Ag(111). The feature at 119 K represents molecular desorption of physisorbed vinyl chloride in a first-order desorption process. The 142 K feature at low coverage represents molecular desorption of vinyl chloride bound more tightly to the Ag surface due to the presence of coadsorbed Cl. The feature appearing at 150–180 K, depending on coverage, is the second-order vinyl plus chlorine recombinative desorption. The feature appearing in Figure 3 at 249 K is the molecular desorption of 1,3-butadiene resulting from the combination reaction of two adsorbed vinyl species.

B. 1,3-butadiene Formation. 1. Kinetic Parameters. The TDS curve in Figure 3 for the mass 54 parent peak of 1,3-butadiene is acquired following 266 nm laser irradiation (1.8 mJ/pulse with a 20 Hz repetition rate for 44 min and a fluence of 7.2×10^{19} photons/cm²) of 0.50 ML vinyl chloride. The kinetic parameters of the recombination reaction may be determined from a fitting of the TDS curve, starting with the Polanyi–Wigner rate equation and using the procedure similar to that of Koel and co-workers.²³ The general Polanyi–Wigner

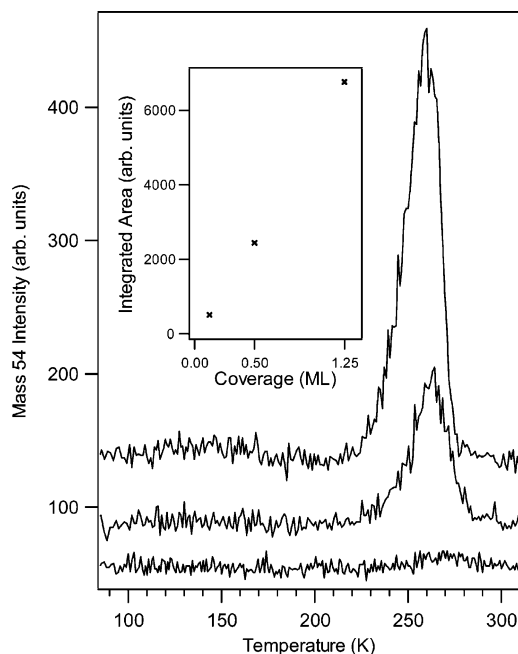


Figure 4. TDS indicating 1,3-butadiene formation following 266 nm irradiation (of less than 2 mJ/pulse, 20 Hz, and approximately equal fluence of 1×10^{19} photons/cm²) of vinyl chloride on Ag(111) with coverages of 1.25, 0.50, and 0.125 ML (top to bottom). The inset shows the integrated area of 1,3-butadiene formed in post-lase TDS.

equation for two surface species, when applied to two identical surface species as in the C_2H_3 plus C_2H_3 combination reaction, reduces to $\text{rate} = d\theta/dT = (\nu^n/\beta)(\theta^n) \exp(-E_a/RT)$, with coverage θ , desorption order n , prefactor ν , and activation energy E_a . The C_2H_3 coverage θ can be related to the detected number of desorbing C_4H_6 molecules by a factor of 2. E_a is the desorption activation energy, which for C_2H_3 plus C_2H_3 on the surface is actually the activation energy for the overall C_4H_6 formation reaction, since this combination-desorption peak occurs at 249 K, which is 83 K higher than the desorption temperature (166 K) of molecularly adsorbed 1,3-butadiene in our chamber. The $\ln(R/\theta^n)$ versus $1/T$ plots in the Figure 3 inset are obtained by integrating the TDS curve to give C_2H_3 coverage as a function of temperature and then displayed with a range of n values in half integers. This plot gives a straight line fit for the correct reaction order n . As shown in the Figure 3 inset, the best desorption model is a first-order process ($n = 1$) where the straight line yields the activation energy of 10.4 kcal/mol and prefactor of 1.1×10^8 s⁻¹ as determined from the slope and intercept, respectively. The first-order character of the bimolecular C_2H_3 plus C_2H_3 surface combination reaction is not intuitive but not uncommon, as previous research on several similar surface reactions yields second-order reactions in some cases and first-order reactions in others.²⁴

2. Coverage, Fluence, and Wavelength Dependence. Irradiating different initial coverages of vinyl chloride produces different post-irradiation quantities of 1,3-butadiene. Figure 4 shows TDS curves following irradiation with 266 nm light of three different coverages. The top curve is 1.25 ML with 8.5×10^{18} photons/cm² fluence, the middle curve is 0.50 ML with 1.2×10^{19} photons/cm², and the bottom curve is 0.125 ML with 9.3×10^{18} photons/cm². The inset shows the quantity of 1,3-butadiene detected from the three cases linearly normalized to the fluence of 10^{19} photons/cm².

Irradiation with different fluences produces different post-irradiation TDS quantities of 1,3-butadiene as well. Figure 5 shows TDS curves following irradiation of 0.50 ML vinyl

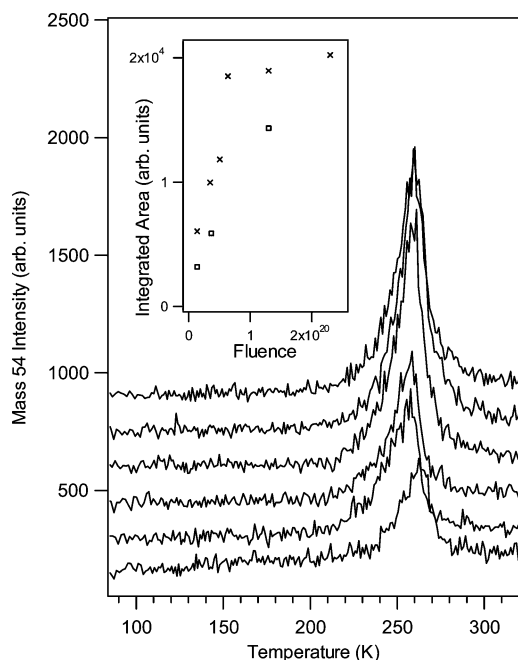


Figure 5. TDS indicating 1,3-butadiene formation following 266 nm irradiation of 0.50 ML vinyl chloride on Ag(111). Fluence (top to bottom) is 2.3×10^{20} , 1.3×10^{20} , 6.4×10^{19} , 5.1×10^{19} , 3.5×10^{19} , and 1.4×10^{19} photons/cm². The inset shows the integrated area of the 1,3-butadiene peak for two sets of data. The data points marked by a cross (×) are for experiments described above. The data points marked by a square (□) are for three experiments performed, under identical irradiation conditions as above, with 0.03 ML Cl preadsorbed on Ag(111) before dosing with vinyl chloride.

chloride with varying fluence. The inset shows the relationship between fluence and quantity of post-irradiation 1,3-butadiene produced under two different initial conditions. The first condition has data points marked as a cross (×), which result from irradiation of vinyl chloride adsorbed on a clean Ag(111) surface. As expected, 1,3-butadiene production appears linearly proportional to fluence initially, but the rate of increase slows down at higher fluences. The second condition has three data points marked with a square (□), which are obtained when the surface has 0.03 ML of Cl preadsorbed on the Ag(111). Note that in each of the three cases with preadsorbed Cl, the amount of 1,3-butadiene produced in post-irradiation TDS is less than the corresponding experiments without preadsorbed Cl. From these results, it appears that preadsorbed Cl inhibits the formation of 1,3-butadiene.

TDS curves following irradiation with lower photon energy of 355 nm light also indicate 1,3-butadiene production. Figure 6 shows TDS curves following irradiation of 0.50 ML vinyl chloride with 355 nm laser light of varying fluence. The quantity of 1,3-butadiene produced with 355 nm laser light, even with 10 times the fluence, is significantly less than that with 266 nm laser light. As with the case of irradiation with 266 nm laser light and constant initial vinyl chloride coverage, 1,3-butadiene production resulting from irradiation with 355 nm laser light appears to increase with higher fluence. In addition, we found that irradiating physisorbed vinyl chloride with 532 nm laser light, even with fluences 1000 times greater than the 266 and 355 nm experiments, produces no measurable post-irradiation TDS desorption peak for 1,3-butadiene.

IV. Discussion

A. Photodissociation Mechanism. The photoinduced dissociation of vinyl chloride adsorbed on Ag(111) we observe

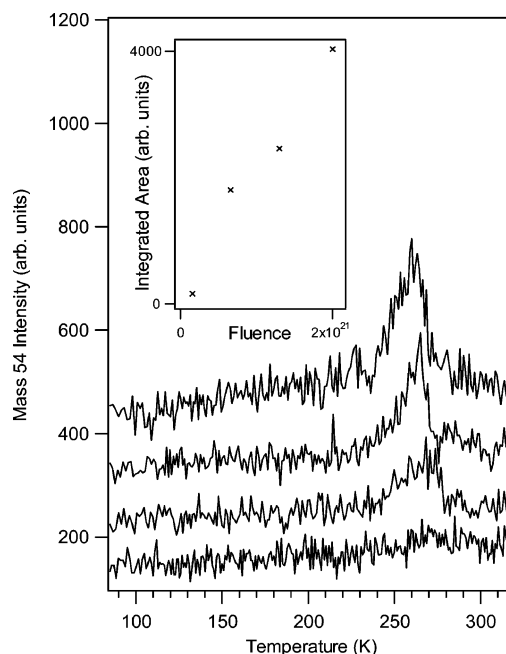


Figure 6. TDS indicating 1,3-butadiene formation following 355 nm irradiation of 0.50 ML vinyl chloride on Ag(111). Fluence (top to bottom) is 2.0×10^{21} , 1.3×10^{21} , 6.6×10^{20} , and 1.6×10^{20} photons/cm². The inset shows the integrated area of 1,3-butadiene formed in post-lase TDS.

should not be a result of direct photon absorption by physisorbed vinyl chloride. Ultraviolet photodissociation of gas-phase vinyl chloride has been well established. The maximum efficiency of absorption–dissociation combined occurs at about 185 nm with no photodissociation detected at wavelengths longer than 220 nm (5.64 eV).^{25–28} As shown in our previous studies, physisorbed vinyl chloride is virtually unperturbed with respect to its gas-phase properties and therefore should show similar photodissociation character as gas-phase vinyl chloride.⁹ The highest photon-energy light used in our experiments is 266 nm (4.66 eV), which is 0.98 eV less than the minimum required for gas-phase photodissociation. Significantly, the substantially less energetic 355 nm (3.49 eV) light also causes dissociation of adsorbed vinyl chloride. Since the data do not support direct photon-absorption induced dissociation, we therefore examine if the dissociation is through a substrate mediated process involving dissociative electron attachment (DEA).

There have been several experimental and theoretical DEA studies of gas-phase vinyl chloride.^{10–14,28,29} Experimental evidence indicates that gas-phase vinyl chloride has a low energy resonance anion state at about 1.2–1.3 eV above the ground state with a cross section of 3.5×10^{-17} cm². The lowest energy anion state decomposes predominately into Cl[−] and the neutral vinyl radical. This state arises with the additional electron in the LUMO of vinyl chloride, the $\pi^*(CC)$ MO.¹¹ Ab initio calculations show the lowest energy resonance π^* MO at 1.29 eV above the ground state. The next lowest resonance state is the $\sigma^*(CCl)$ orbital at 2.9 eV above the ground state, which is observed as about 40 times less intense in experiments than the π^* resonance.^{10,13}

The stability of the anion state of the gas-phase molecule depends on the strength of the bond to be broken. In chloroalkanes, electron capture into the $\sigma^*(CCl)$ orbital with a bond order of 0.5 leads to dissociation. In chloroalkenes, though, the capture of an electron in the π^* orbital does not lead to breaking of the anion's C=C bond with a bond order of 1.5. The π^* excitation, however, results in dissociation into Cl[−] and the

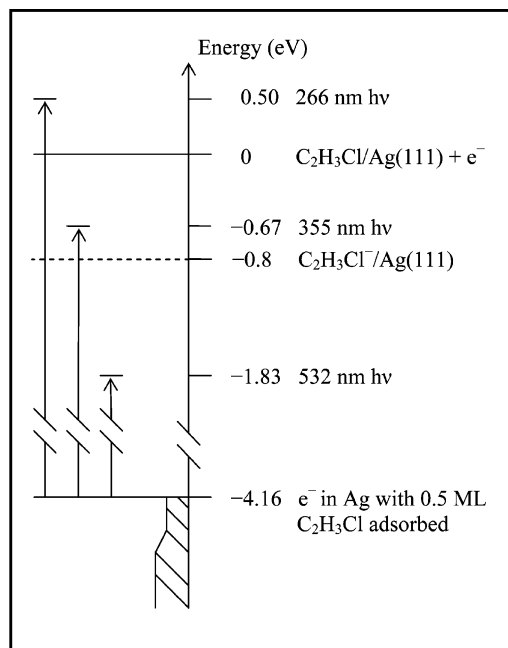


Figure 7. Energy diagram for photon induced vertical electron transfer from Ag(111) to the physisorbed vinyl chloride.

alkene radical through an electronic predissociation process. For gas-phase vinyl chloride, the DEA cross section is very large for electrons with energies near the π^* resonance, leading to the dissociation of the C–Cl bond but not the C=C bond, while essentially no dissociation is induced near the σ^* resonance.¹⁴ Electron capture at 1.29 eV into the $\pi^*(CC)$ orbital of vinyl chloride forms the $^2\Pi$ anion state.¹¹ The gas-phase vinyl chloride anion is distorted from a planar C_s to a C_1 structure by the C–Cl out-of-plane deformation, which happens immediately after anion formation by electron capture into the π^* orbital. The deformation vibronically mixes the Σ and Π states and allows the $^2\Pi$ anion access to the $^2\Sigma$ repulsive dissociation state resulting in $C_2H_3 + Cl^-$.^{10,13}

Since the physisorbed vinyl chloride is relatively unperturbed from its gas-phase properties, it is reasonable to consider such a gas-phase DEA mechanism for the physisorbed vinyl chloride. We propose that the photoexcited electrons in the metal may cause DEA of adsorbed vinyl chloride. Similar to the gas-phase dissociation, the Cl^- and vinyl fragments in the physisorbed system are also most efficiently produced through the capture of the incident electron into the low-lying unoccupied π^* orbital of the physisorbed vinyl chloride.

The feasibility of the DEA process for vinyl chloride physisorbed on Ag(111) is illustrated by the energy diagram in Figure 7. Zero energy in this diagram is defined as the energy of vinyl chloride adsorbed on Ag(111) plus free electrons with zero kinetic energy. In setting the relative energies of the neutral versus anion states, we first estimate the substrate work function (Φ) of Ag(111) with vinyl chloride adsorbed on the surface. Although there is some dispute in the literature, we use the value of 4.46 eV as the clean Ag(111) work function.³⁰ The physisorbed vinyl chloride is oriented with the molecular plane parallel to the surface,⁹ so even though vinyl chloride has a permanent dipole moment of 1.4 D, there should only be a slight reduction in the work function when the vinyl chloride is physisorbed on clean surface Ag(111). The work function with vinyl chloride adsorbed on Ag(111) can be estimated by comparisons with other similar systems. For example, when monolayer C_6H_5Cl weakly chemisorbs on Ag(111) with the

molecular plane parallel to the surface, $\Delta\Phi$ is -0.65 eV.³¹ For monolayer physisorbed C_2H_5Cl and CH_3Cl on Ag(111), $\Delta\Phi$ is -0.95 and -0.8 eV, respectively.³ Monolayer physisorbed C_2H_5Br and *cis*- $CHCl=CHCl$ on Cu(100) have $\Delta\Phi$ as -0.325 and -0.45 eV, respectively.^{32,33} The slight reduction in work function appears typical upon adsorption of polar halogenated hydrocarbons on metal surfaces.^{32,34} For 0.50 ML vinyl chloride adsorbed on Ag(111), not the full monolayer for which the values cited above were determined, we estimate the reduction in work function as -0.3 eV. Consequently, the work function for the 0.50 ML vinyl chloride adsorbed on Ag(111) is estimated as $\Phi[C_2H_3Cl/Ag(111)] = 4.16$ eV.

The π^* resonance is placed at 1.3 eV above the ground-state energy of gaseous vinyl chloride. Adding the physisorption energy of 0.3 eV of vinyl chloride on Ag(111) to the anion state energy, the gaseous vinyl chloride negative ion is placed 1.6 eV above zero. The adsorption energy of the anion is determined by considering stabilization energies due to image charge attraction (E_{im}), stabilization by electronic polarization of the surrounding molecular medium (E_{pol}), and additional energy shifts specific to the ion in the adsorbed state and not present in the gas phase (δ), such as exchange/correlation interactions between the extra electron and the substrate electron density. The adsorption energy of the anion is then $E_{ad}(C_2H_3Cl^-) = E_g(C_2H_3Cl) - E_{im} - E_{pol} - \delta$. E_{im} is inversely proportional to the dielectric constant of the medium between the ion and the surface, ϵ , and the distance of the external charge from the surface plane, z , in that $E_{im} = e^2/4z = 3.6/z$ eV.³⁵ The polarization energy (E_{pol}) is estimated as some fraction, χ , of the ground-state polarization energy of the solvated anion, P^- , so that $E_{pol} = \chi P^-$.³⁵ The fraction χ is ~ 0.8 for bulk multilayers, ~ 0.53 for the topmost layer of the multilayer, and ~ 0.33 for monolayers and below.³⁵ P^- is inversely related to the radius of the anion, r , and related to the dielectric constant of the solvent molecule, ϵ , as $P^- = e^2/2r\{1 - (1/\epsilon)\}$. With χ set as 0.33, ϵ (dielectric constant of the vinyl chloride solvent) as 6.26,³⁶ z estimated as 3 Å for the physisorbed system, δ considered the same as the adsorption energy of the physisorbed molecule, and r estimated at 3.3 Å, we calculate $E_{im} \sim 1.2$ eV and $E_{pol} \sim 0.9$ eV. The vinyl chloride anion $C_2H_3Cl^-$ on Ag(111) is placed at -0.8 eV below vacuum.

The minimum photon energy required for excitation of electrons at the Fermi level to access the anion state is approximately 3.4 eV (365 nm). As shown in Figure 7, 266 and 355 nm photons are sufficiently energetic to excite hot electrons with sufficient energy to access the anion state, while 532 nm light is not. These energetics are consistent with our experimental observations of vinyl chloride photodissociation, as indicated by the presence (irradiation with 266 and 355 nm light) or absence (irradiation with 532 nm light) of 1,3-butadiene in the post-irradiation TDS curves.

We now comment on the effect of adsorbed Cl on the energetics of the electron attachment process. The adsorption of Cl to the surface significantly changes the work function, even at very low coverage. Monolayer coverage of Cl on Ag(111), which is 1 Cl adsorbed in a 3-fold hollow site among 3 Ag atoms, increases the work function by 1.8 eV. With as little as 0.1 ML Cl on Ag(111), the work function increases by about 0.2 eV.^{37,38} The manifestation of this adsorbed Cl effect is the leveling off of 1,3-butadiene production as shown with the cross (×) data points in Figure 5. We propose that as the experiment continues and more vinyl chloride is photodissociated, the amount of Cl adsorbed to the surface increases. With increasing Cl on the surface, the work function of the surface also increases.

TABLE 1: Photodissociation Cross Section^a

| λ_{hv} (eV) | fluence (10^{19} photons/cm ²) | σ_{I} (10^{-21} cm ²) | σ_{II} (10^{-21} cm ²) |
|-------------------------------|--|---|--|
| 532 nm (2.33 eV) | 200 000 | not observed | not observed |
| 355 nm (3.49 eV) | 16 | 0.013 | 0.14 |
| | 66 | 0.036 | 0.39 |
| | 130 | 0.025 | 0.27 |
| | 200 | 0.027 | .029 |
| 266 nm (4.66 eV) | 1.4 | 6.9 [3.0] | 13 [5.7] |
| | 3.5 | 4.4 [2.0] | 8.3 [3.8] |
| | 5.1 | 3.0 | 5.7 |
| | 6.4 | 3.8 | 7.2 |
| | 13 | 1.9 [1.5] | 3.6 [2.8] |
| | 23 | 1.1 | 2.1 |

^a Photodissociation cross sections of 0.5 ML vinyl chloride on Ag(111) without preadsorption of Cl and with 0.03 ML Cl preadsorbed (numbers in square brackets). Two cross sections are reported: σ_{I} is a phenomenological cross section and σ_{II} is a cross section for substrate photoexcited electrons.

Consequently, the amount of hot electrons with sufficient energy to access the dissociative anionic state is reduced, with the result of less vinyl chloride dissociation as the experiment continues to high fluence levels. This explanation is consistent with the comparison between the square (\square) data and the cross (x) data: at the same fluence there is less 1,3-butadiene production when the surface has preadsorbed Cl versus when the experiment starts with a clean Cl surface.

B. Photodissociation Cross Section. The experimentally determined quantity of butadiene produced as a function of incident light fluence allows the determination of the cross section of the photodissociation process. This phenomenological cross section, σ_{I} , is based on the fluence (the total number of photons per cm² reaching the surface noted as N_{hv} , the number of vinyl chloride species initially adsorbed per cm² of surface N_{VCl} , and the number density of vinyl species generated on the surface, N_{V} , after vinyl chloride dissociation). Alternatively we can define a substrate photoexcited electron cross section σ_{II} based on the total number of photoexcited electrons generated from the photons per cm² actually absorbed by the Ag(111) surface, N_{hvabs} . The two cross sections are then defined by the equations $\sigma_{\text{I}} = N_{\text{V}}/(N_{\text{hv}} \cdot N_{\text{VCl}})$ and $\sigma_{\text{II}} = N_{\text{V}}/(N_{\text{hvabs}} \cdot N_{\text{VCl}})$.

The number of vinyl chloride molecules initially adsorbed on the Ag surface, N_{VCl} , has been estimated in our previous study based on the adsorption geometry of the molecule on Ag(111).⁹ The number of C₂H₃ adsorbed to the surface after dissociation, N_{V} , is determined as twice the number of 1,3-butadiene molecules produced in post-irradiation TDS, which is calibrated with a series of TDS curves for known 1,3-butadiene coverage dosed in our chamber. The total number of photons incident on unit surface area, N_{hv} , is determined by the laser pulse energy, repetition rate, overall duration of irradiation, and the illuminated surface area. The number of photons absorbed by the Ag surface, N_{hvabs} , is calculated based on the Ag reflectivity for the specific photon wavelength at 45° incidence angle. Table 1 lists the cross sections and their ratio (σ_{I} , σ_{II} , and $\sigma_{\text{I}}/\sigma_{\text{II}}$) for 532, 355, and 266 nm light at various incident fluences for surfaces with or without preadsorbed Cl.

Photodissociation of vinyl chloride depends on generation of hot electrons in the metal substrate that are able to access the physisorbed vinyl chloride π^* orbital and ultimately cause dissociation. The generation of hot electrons results from photon absorption by the metal substrate. The number of vinyl chloride molecules these hot electrons are able to access depends on both the coverage of vinyl chloride and the efficiency of the hot electrons to reach the Ag surface.³⁹ For the excited carriers that

do reach the surface to tunnel onto the vinyl chloride in a DEA process, there is a surface potential barrier to overcome. Furthermore, the molecular anion may either dissociate or relinquish the electron and desorb as a neutral molecule. The overall cross section σ_{I} includes the effects of photoexcitation efficiency, the fraction of photoexcited electrons reaching the surface, the number of electrons attached to the molecules, and the photodissociation efficiency, while σ_{II} reflects the combined transport, tunneling, and dissociation efficiency.

With a photon energy of 355 nm (3.49 eV), only substrate electrons near the Fermi level have enough energy to tunnel to the vinyl chloride and form the transient anion state. Ag has a relatively constant density of states from the Fermi level down to about 3.9 eV below, where the d bands begin with a sharp increase in density of states to about 6.9 eV below the Fermi level.^{40–42} Neither the 266 nm nor the 355 nm light can access this higher density of states of the d bands. Both photon energies allow access only to the relatively constant density of states just below the Fermi level. As the 266 nm light enables more hot electrons to be energetically sufficient for DEA of vinyl chloride than the 355 nm light, it is expected that the cross section σ_{I} is larger for 266 nm versus 355 nm light, as reflected in Table 1. The electrons with more energy are expected to have higher tunneling efficiency to reach the adsorbed molecule as well as causing its more efficient dissociation. As 266 nm light produces more energetic electrons, the cross sections σ_{II} are larger for 266 nm as well.

The cross sections appear to increase with fluence initially but decrease at much higher fluence. This behavior is identical for both 355 and 266 nm. We attribute this to the hot electron density dependence in the electron relaxation and diffusion rates. It has been observed that the charge screening effect causes both the hot electron relaxation⁴³ and diffusion⁴⁴ rates to decrease. At much higher density the diffusion rate increases again because of the occupation of the higher kinetic energy states. Slower relaxation and diffusion retains the hot electrons near the surface longer and would result in a more efficient photodissociation process. The decrease of the cross sections at very high fluences likely is due to a combination of the increased diffusion and saturation due to a finite number of adsorbed molecules.

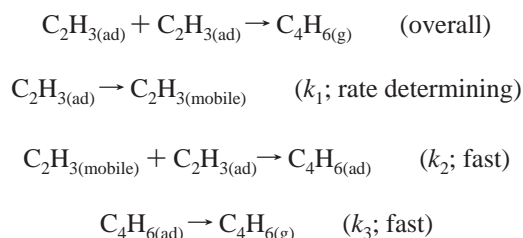
The effect of surface Cl adsorption on vinyl chloride photochemistry is quantitatively displayed in the calculated cross sections determined for the case of an initially clean Ag(111) surface versus the case of 0.03 ML of preadsorbed Cl on the surface. Consistent with the previous discussion of how adsorbed Cl increases the work function of the Ag(111) surface, one expects that with preadsorbed Cl there will be fewer hot electrons able to reach the π^* orbital and form the transient anion. With fewer transient anions formed, one expects less dissociation and a lower dissociation cross section for the case of preadsorbed Cl versus the case of a clean surface. The calculated cross sections are consistent with this discussion as the cross sections measured for 0.50 ML vinyl chloride dosed on the surface with 0.03 ML of Cl preadsorbed are less than the cross sections without preadsorbed Cl.

C. Isotope Effect. The proposed substrate electron mediated dissociation mechanism is supported by the isotope effect observed in Figure 1. As discussed previously, TDS curves in Figure 1 show that C₂H₃³⁵Cl is 1.2 times more likely to desorb during irradiation than C₂H₃³⁷Cl. This light versus heavy isotope effect has been reported previously in the study of electron stimulated desorption of oxygen on tungsten and of phonon versus electron-mediated desorption of carbon monoxide on

ruthenium.^{45,46} In these studies, the lighter isotope species more readily desorbs than the heavier isotope species.

The adsorbed anion has a short lifetime of 10^{-15} to 10^{-13} s,^{7,47} during which time it is either quenched to the neutral or dissociates on a repulsive potential energy surface. Once the anion is formed, it is attracted to its surface image charge, moves closer toward the surface, and thus has a surface-to-adsorbate distance that is shorter than that of the neutral. In the adsorbate–substrate system, the anion has a higher potential energy than the neutral species. When the negative charge of the undissociated anion returns back to the metal substrate, the adsorbate becomes a neutral species displaced from its equilibrium position and has increased kinetic energy. As a result of the displacement, desorption of the neutral species may occur. The yield of desorption depends on the competition relaxation of the increased kinetic energy and desorption. For anions with the same charge, lighter species ($\text{C}_2\text{H}_3^{35}\text{Cl}$) are accelerated faster toward the image charge in the metal than heavier species ($\text{C}_2\text{H}_3^{37}\text{Cl}$). As a result, lighter species are further displaced from the equilibrium position and are therefore more likely to desorb from the surface before the energy is relaxed into the substrate than are the heavier species. This light versus heavy isotope effect is consistent with our data as presented in Figure 1.

D. Diffusion-Limited C_2H_3 Recombination on Ag(111). The photochemical product C_2H_3 is chemisorbed on Ag(111) so it does not diffuse freely on the surface at low temperatures. The C_2H_3 plus C_2H_3 combination reaction, on the other hand, requires a physical encounter of one C_2H_3 with another. The combination reaction rate therefore is expected to be diffusion limited. The mechanism below may account for the observed first-order kinetics of the 1,3-butadiene production.



Both the combination reaction and desorption rates are expected to be much faster than the diffusion rate. As with similar adsorbate–metal substrate systems,⁴⁸ it is expected that once the surface temperature becomes high enough to produce $\text{C}_2\text{H}_{3(\text{mobile})}$, the $\text{C}_2\text{H}_{3(\text{mobile})}$ quickly diffuses to find a $\text{C}_2\text{H}_{3(\text{ad})}$ with which to react, thus the fast k_2 . Once $\text{C}_4\text{H}_{6(\text{ad})}$ is formed at 249 K, it immediately desorbs as the surface temperature is 83 K higher than the desorption temperature of molecularly adsorbed 1,3-butadiene as dosed in our chamber, thus giving a fast k_3 . The overall rate is then determined by the relatively slow k_1 . The overall C_2H_3 plus C_2H_3 combination reaction rate is thus described as rate = $k_1[\text{C}_2\text{H}_{3(\text{ad})}]$ with a surface diffusion barrier as activation energy.

Seebauer and Allen described several trends of surface diffusion from the experimental observations of over 500 adsorbate–surface systems in a recent review.⁴⁸ The surface diffusion rate D is shown to be related to a diffusion pre-factor (D_0) and diffusion activation energy (E_d) so that $D = D_0 \exp(-E_d/kT)$. For nonmetal adsorbates on metal substrates, D_0 values have a mean of $1 \times 10^{-3} \text{ cm}^2/\text{s}$, corresponding to jump attempt frequencies of $\sim 10^{12}/\text{s}$, and that the ratio of the E_d to the desorption activation energy E_a , E_d/E_a , has an average value of 0.23 with two-thirds of the reported values in the range 0.13 and 0.33.

Consider the cases of C_2H_3 and C_4H_6 on both Ag(111) and Cl–Ag(111). C_4H_6 adsorbs on Ag(111) molecularly with an estimated binding energy of 10 kcal/mol. The bond enthalpy for C_4H_6 to $\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3$ in the gas phase is 99 kcal/mol.⁴⁹ If following the recombination reaction there is sufficient energy to desorb the C_4H_6 product, the binding energy of C_2H_3 on Ag(111) is estimated to be no more than 49.5 kcal/mol. Using the findings for the typical E_d/E_a ratios, we estimate the diffusion activation energy as somewhat smaller than 11.4 kcal/mol (0.23×49.5). This value is close to the activation energy of 10.4 kcal/mol that we have measured for C_4H_6 production in post-irradiation TDS, but smaller than the 15.2 kcal/mol measured by White and co-workers for thermally activated C_2H_3 (C_2H_3 formed by irradiating adsorbed C_2H_4 with 5–57 eV electrons emitted from the QMS filament) plus C_2H_3 combination reaction to form C_4H_6 on Ag(111).²⁴

V. Summary

In this study we have found that 266 and 355 nm photons induce dissociation of vinyl chloride physisorbed on Ag(111), while the 532 nm photons merely induce molecular desorption. The photon-induced dissociation of vinyl chloride into adsorbed C_2H_3 and Cl is not by direct photon absorption by the molecule, but rather through a substrate mediated mechanism. This system provides another example, in addition to formaldehyde on Ag(111), illustrating that *physisorbed* molecules with known unstable negative ion state can undergo reactions induced through electrons excited in the substrate. But unlike formaldehyde, whose photochemical fragments induce polymerization on the surface,⁹ vinyl chloride photofragments simply recombine on the surface without polymerization.

Photoexcited substrate electrons with sufficient energy may tunnel onto adsorbed vinyl chloride and form vinyl chloride anions, which may then quench to the neutral or dissociate. This mechanism can be constructed based on the reported dissociative negative ion states of vinyl chloride in the gas phase. In this mechanism, the unstable negative ion state of vinyl chloride adsorbed on Ag(111) is estimated at 0.8 eV below vacuum, consistent with the observed photon wavelength-dependent dissociation behavior. This mechanism is also consistent with the observed isotope effect in 1,3-butadiene production from recombination of the adsorbed vinyl in post-irradiation TDS, as well as with the observed reduced 1,3-butadiene production on Ag(111) with coadsorbed Cl. The presence of Cl on Ag(111) increases the work function of the substrate and therefore increases the energy of the adsorbed vinyl chloride anion state and the threshold for substrate electron attachment. Furthermore, on the post-irradiation surface, C_2H_3 combination (forming butadiene) reaction appears to proceed through a diffusion-limited, first-order, process with activation energy of 10.4 kcal/mol.

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