Surface Chemistry of Chloroiodomethane, Coadsorbed with H and O, on Pt(111)


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Abstract: Using temperature programmed desorption (TPD), predosed oxygen TPD (POTPD), high-resolution electron energy loss spectroscopy (HREELS), and Auger electron and X-ray photoelectron spectroscopy (AES and XPS), we have investigated the chemistry of chloroiodomethane (ClCH2I) dosed onto clean, D-covered and O-covered Pt(111). At or below 100 K, ClCH2I adsorbs moleculely on all these surfaces. While ClCH2I in physisorbed multilayers desorbs reversibly, a significant portion in the first monolayer dissociates during heating. In the absence of D and O, dissociation begins with C–I bond cleavage at ~150 K. Once the C–I bond breaks, several competitive reactions take place below 260 K: (1) hydrogenation of CH2Cl(a) to form CH3Cl(g) beginning near 150 K, (2) Cl–CH2(a) bond cleavage to form Cl(a) and CH2(a) above 170 K, (3) dehydrogenation of CH3(a) to CH(a) beginning near 180 K and increasing rapidly above 200 K, (4) hydrogenation of CH2(a) to CH4(g) above 170 K, and (5) HCl and H2 formation and desorption above 200 K. At 260 K, the surface species are identified as (a), CH(a), Cl(a), and a small quantity (~0.02 ML) of CH2(a). The remaining CH2(a) reacts with itself and Cl(a) to form HCl(g), HCl(g), and CH(a) at 360 K. Cl(a) remnants react with CH(a) at 415 K, producing HCl(g) and CCH(a). The residual CH(a) fragments react at 520 K, yielding H2(g), C(a), and more CCH(a). Finally, dehydrogenation of CCH(a) occurs between 550 and 700 K, releasing H2 and leaving carbon, presumably clustered. Coadsorbed D atoms weaken the bonding between ClCH2I and the surface, decrease the amount of CCH2I dissociating, and suppress the complete decomposition to carbon for those ClCH2I molecules that do dissociate. In TPD with coadsorbed D, besides the addition products (i.e., CH3D, C2H5D, and CH2DCI), there are also H–D exchange products for methane (i.e., CHD2 and CD3), but not for methyl chloride (i.e., no CH2DCl and CD3Cl). Coadsorbed O atoms attenuate slightly the dissociation of ClCH2I, but strengthen its bonding with the surface. With increasing O coverage, the yields of CH4, CH3Cl, H2 and HCl (reaction products found in the absence of O(a)) decrease; other reaction products, H2O, CO2, CO, CH2O, and CH2Cl2, appear and increase. To our knowledge, this is the first report of formaldehyde produced by the oxidation of a CH2 precursor on Pt(111). Reaction paths are discussed, as are the effects of coadsorbed halogen atoms on hydrogenation, C–C coupling, and oxidation of CH4.

1. Introduction

The surface chemistry, including photochemistry, of halogenated hydrocarbons is receiving considerable attention for several reasons. First, these molecules serve as important precursors for preparing surface hydrocarbon intermediates. Because carbon–halogen (C–X) bonds (except C–F) are typically weaker than C–H and C–C bonds and because they can be selectively dissociated through irradiation with photons or low energy electrons, these molecules are viable precursors to selected hydrocarbon fragments. Both thermal and nonthermal methods have been employed. The surface chemistry of these fragments, of great importance in hydrocarbon catalysis, can then be studied in a great detail. Second, halogenated hydrocarbons or halocarbons are well-known environmental pollutants, and their fundamental chemistry on solid surfaces is relevant to environmental protection and cleanup technologies. Third, halogenated hydrocarbons are important agents for the processing of silicon-based electronic materials. We have studied the surface chemistry of chloroiodomethane (ClCH2I) on Pt(111), with and without coadsorbed atomic hydrogen or oxygen. One motivation was to study the thermal activation of C–Cl bonds, which plays an important role in the catalytic destruction of halogenated hydrocarbons. For simple alkyl chlorides adsorbed on Pt(111), raising the surface temperature typically results in the desorption of parent molecules; the C–Cl bonds remain intact. Because alkyl iodides

decompose thermally on Pt(111) at low temperatures and because the C–I bond energy (56 kcal/mol) is much lower than the C–Cl bond (84 kcal/mol), thermal dissociation of ClICl–I may generate stable surface CICl₂. In such fragments, the dissociation of C–Cl is typically competitive with C–H and C–C cleavage, thus, study of thermal dissociation of C–Cl bonds becomes possible by first generating the Cl-containing hydrocarbon fragments. We find, as expected, that dissociation of adsorbed CICl₂ begins with C–I bond cleavage commencing at 150 K. The dissociation of the C–Cl bonds in the resulting CICl₂ fragments starts at 170 K and is kinetically competitive with hydrogenation of CIC₂H.

A second motivation was to study the surface chemistry of methylene (CH₂) on Pt(111) using ClICl₂ as a precursor. CH₂ is an important intermediate in Fischer–Tropsch synthesis and catalytic conversion of hydrocarbons. While the chemistry of methyl (CH₃) fragments on Pt(111), derived from thermal and nonthermal dissociation of methyl halides and other CH₃-bearing molecules, has been extensively studied, less is known about the surface chemistry of CH₂. Berlozovitz et al., using TPD, studied diazomethane (CH₂N₂) on Pt(111), with and without coadsorbed hydrogen or oxygen. There was evidence that CH₂N₂ adsorbed dissociatively at 110 K, producing surface CH₂ and gaseous N₂. In thermal desorption, H₂, CH₄, and C₂H₄ were observed with or without coadsorbed H. On O-covered Pt(111), CO, CO₂, and H₂O were observed in TPD. For CH₃CO₂ ketene, on Pt(111), one of the proposed reaction pathways is dissociation to form transient CH₂ fragments that decompose to CH and H, hydrogenate to CH₄, and react with undissociated CH₂CO to form C₂H₄. These methyl radicals do not accumulate to concentrations observable to HREELS.

The chemistry of CH₂ on other metal surfaces has been reported. On Ag(111), CH₂ desorbed from thermal dissociation of adsorbed CH₂Cl₂, recombines exclusively to form C₂H₄. On Cu(110), the same conclusion was reached using CH₂Cl₂. On Pd(100), CH₂ desorbed from CH₂Cl₂ reacts to form CH₄ and C₂H₄. For CH₂Cl₂ on Al, CH₂ radicals and C₂H₄ were found in TPD. On polycrystalline Co and Ni, adsorbed CH₂Cl₂ dissociates at ~180 K to form CH₂, which decomposes in steps to CH and C at elevated temperatures. In the diazine–Pd(110) system, surface CH₂ formed at ~140 K, reacts at ~200 K, yielding gaseous CH₄ and C₂H₄. On Ru(001), HREELS data indicates that adsorption of diazomethane at 80 K gives surface CH₂ which rearranges upon heating to 280 K, to a mixture of CH₂, CH₄, and C₂H₄. This mixture decomposes to C and H upon heating to 500 K. For CH₂CO on Ru(001), a fraction of adsorbed CH₂CO dissociates to CH₂ which reacts, presumably via CH₂H₂, to form CCH₃(a), ethylidyne. CH₃ has also been identified in several other systems.

In this study, we observe chemistry, in the presence of coadsorbed I and Cl, of CH₂ on Pt(111). Compared to CH₂Cl₂ on Pt(111), there are both similarities and differences which are related to the presence of halogens. The primary reaction of CH₂ on Pt(111) is dehydrogenation to form adsorbed methylidyne, CH(a), and coincidental hydrogenation to gaseous methane, CH₄(g). This occurs at a much lower temperature, ca. 210 K, than for CH₂(a), ca. 280 K. The coupling of CH₂(a) to form C₂H₄ found on other metal surfaces, e.g., Ag(111), Cu(110), Al, Pd(110), and Pd(100), was not observed in this study; it has, however, been reported for CH₂Cl₂ on Pt(111). In the presence of coadsorbed D, methane formation is enhanced and there is a H-for-D exchange reaction involving C–H bonds. In the presence of coadsorbed O, besides H₂O, CO, and CO₂, formaldehyde (H₂CO) is produced during TPD. In addition, there is a new reaction channel—chlorination to form CH₂Cl₃, which does not occur in the absence of O.

2. Experimental Section

The experiments were carried out in two separate ultrahigh-vacuum chambers; both had a base pressure of (3–7) × 10⁻¹⁰ Torr. One (machine I) was equipped with temperature programmed desorption (TPD), Auger electron spectroscopy (AES), and Fourier transform mass spectroscopy (FTMS) (not used in this study) facilities and has been described elsewhere. The second chamber (machine II) had high-resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS), and TPD facilities; a more detailed description has been given previously. The TPD and AES data presented in this paper were obtained from machine I and the HREELS and XPS data from machine II.

The Pt(111) crystal was cleaned by sequences of Ar ion sputtering at 300 K, oxidation at 800 K, and annealing at 1150 K; cleanliness was confirmed by AES or XPS. The crystal was cooled to 100 K, or slightly below, with liquid nitrogen and was heated resistively at a rate of 6 K/s for TPD (line-of-sight). The substrate temperature was monitored with a chromel-alumel thermocouple spot-welded to the back of the crystal. To prevent electrons, emitted from the QMS filament, away from the surface during line-of-sight TPD, a stainless steel foil with a ~1.5 cm² square hole, covered with 80% transparent mesh, was placed on, but electrically isolated from, the head of the QMS. With the foil floated electrically, no current was measured between the Pt(111) and ground.

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3. Results

3.1. CICH2I on Clean Pt(111). 3.1.1. TPD and AES. For CICH2I adsorbed on clean Pt(111) at 85 K, the subsequent TPD products were H2, CH3, HCl, CH2Cl, I, and parent CICH2I; C2 and higher hydrocarbons were not detectable. AES spectra, recorded after heating the crystal to 1050 K, revealed only a small quantity of adsorbed C. A full description of TPD results is presented below.

Figure 1 shows the TPD spectra of CICH2I for different exposures (dosing time in seconds is indicated on each curve). For exposures of 75 s or less, molecular CICH2I desorption was undetectable, indicating irreversible adsorption. For exposures of 100 s or longer, the CICH2I TPD has peaks at 233 and at 175 K, both of which intensify and saturate at 250 s. Then, a third peak at 160 K appears. This low temperature peak grows continuously with increasing exposure and does not saturate, so we attribute it to a physisorbed multilayer. This agrees with our earlier result: multilayer CICH2I adsorbed on Ag(111) desorbs at about 164 K.19 The 233 K peak is attributed to CICH2I molecules adsorbed in the first monolayer. We attribute the 175 K peak to adsorbed CICH2I influenced by surface iodine. This is justified by the following facts. Heating the surface dosed with CICH2I for 300 s at 85 to 700 K leaves 0.128 ML of atomic iodine and 0.102 ML of carbon on the surface (see below). We cooled this surface to 85 K, dosed CICH2I, and, in the subsequent TPD, found a much more intense CICH2I peak at 175 K than in Figure 1. Evidence (see below) shows that cleavage of C–I bonds, forming I(a), starts at 150 K. The 175 K peak is certainly not due to the influence of surface carbon because there is no evidence for carbon formation below 180 K (see below). Figure 6, which summarizes peak areas as a function of exposure, shows that, for exposures longer than 200 s, the CICH2I TPD area versus dosing time increases linearly, indicating a constant sticking coefficient and reversible adsorption of that CICH2I which desorbs at 160 and 175 K. From Figure 1, we conclude that multilayers begin to form for doses exceeding 160 s.

Figure 2 shows the TPD spectra of one product, CH3Cl. As for the parent, CH2Cl was detected only for exposures exceeding 75 s. For 100 s dose, CH3Cl has a peak at 216 K with a small shoulder at lower temperature. With increasing exposure, the peak intensifies and shifts down to 210 K. The shoulder also intensifies and, for exposures longer than 160 s, becomes an overlapping peak at about 190 K. After dosing CH3Cl at 85 K, the monolayer and multilayer desorbed at 140 and 110 K, respectively, in agreement with earlier reports.14,11,241 The desorption temperature of CH3Cl in Figure 2 is much higher than 140 K, indicating that its desorption is reaction-limited. Based on the fact that, when CICH2I is coadsorbed with D, CH2DCl exceeds CH3Cl in TPD (see section 3.2), we conclude that the formation of CH3Cl involves hydrodegradation of CH2Cl. The CH3Cl TPD peak appears at about 75 s and increases monotonically until it saturates at about 200 s. Saturates exclude the possibility that CH3Cl is an impurity in the CICH2I.

Figure 3 shows the CH3 TPD spectra for the same experimental conditions as Figure 1. Methane first appears at 30 s—a small peak at 235 K. Two peaks at 220 and 270 K appear for a 50 s dose; at 75 s, the 270 K peak saturates and is buried under the tail of the 220 K peak; the latter continues to increase and saturates at 200 s. For exposures of 100 s and longer, there appear, in addition, a shoulder at about 200 K and a small peak at 355 K; both intensify and saturate at 200 s. As shown in Figure 6, the total CH3 TPD area increases above 30 s and saturates at about 200 s.

The formation of CH3 is attributed to dissociation of both C–I and C–Cl bonds and subsequent hydrogenation of the resulting CH2 fragments. This is striking; C–Cl bonds in adsorbed CH2Cl14, C2H2Cl9, and CICH2HBr15 on Pt(111) do not dissociate upon heating. On Ag(111), the Cl–C bond dissociates when CICH2I19, but not CH2I42 and C2H2Cl43, are dosed. Based on the known thermal behavior of alkyl halides on Pt(111) and the fact that C–I bonds are much weaker than C–Cl bonds (54 versus 80 kcal/mol), we propose that the dissociation of CICH2I on Pt(111) begins with cleavage of C–I bond, consistent with XPS data (see section 3.1.2). Dissociation of C–Cl in the resulting CH2Cl becomes competitive, compared to (41) Jo, S. K.; Zhu, X.-Y.; Lennon, D.; White, J. M. Surf. Sci. 1991, 241, 331.
to C\(_2\)H\(_2\)Cl and CH\(_3\)Cl, because CH\(_2\)Cl is much more strongly bound to the substrate. For methyl and ethyl chloride, C–Cl cleavage cannot compete with parent desorption. In our case, the onset temperature of CH\(_2\) desorption suggests that C–Cl dissociation commences at 170 K. While dissociation to CH\(_2\)(a) and Cl(a) is thermodynamically favored (CH\(_2\)Cl(a) → CH\(_2\)(a) + Cl(a), \(\Delta H = -33\) kcal/mol on Pt(111)\(^{44}\)), some CH\(_2\)Cl is hydrogenated to form CH\(_3\)Cl. Clearly, H–CH\(_2\)Cl bond formation and CH\(_2\)–Cl bond dissociation compete kinetically between 170 and 220 K. On Ag(111), since there is no H(a) available, all CH\(_2\)Cl fragments dissociate, and the resulting CH\(_2\) fragments recombine to form ethylene at 218 and 259 K.\(^{19}\)

In two, partly repetitive panels with different vertical scales, Figure 4 shows the TPD spectra of HCl. Unlike the previous three TPD products, HCl grows in from the lowest exposures (Figure 6). At 10 s, i.e., about 5% of the exposure required to begin multilayer growth, the peak is 510 K; for longer doses, it intensifies and shifts to lower temperature, saturating at 130 s with a peak temperature of 415 K. At 20 s, a second peak, 315 K, emerges and shifts downward as the dose increases. There are two peaks, 240 and 265 K, for a 50 s exposure; we interpret the former as connected to the 315 K peak and the latter as arising from a different process. The low temperature peak becomes constant (220 K) for exposures longer than 75 s and its intensity saturates at 200 s. For 100 s, there is a new peak at 360 K; its position remains the same, but its intensity increases up to 200 s. The total HCl TPD area increases with CICH\(_2\)I exposure and, in common with other products, saturates at 200 s dose.

Clearly, HCl TPD is multifaceted. Wagner and Moylan\(^{45}\) have recently studied the adsorption and desorption of HCl on Pt(111). At 90 K, it adsorbs dissociatively; recombination to form HCl dominated the TPD. At very low exposures, HCl desorbed as a single second order peak at about 400 K. At saturation, undissociated HCl desorbed as a major peak at 220 K and a shoulder at about 270 K. A small fraction of H(a) desorbed as H\(_2\), leaving behind a small amount of Cl(a), which desorbed atomically at 960 K. In the presence of preadsorbed H(a), the fraction of Cl(a) which desorbed atomically decreased; the HCl peak at 220 K was still dominant, but the shoulder at 270 was attenuated, and the temperature at which HCl desorption ceased decreased from about 420 to 320 K. Comparing HCl desorption from CICH\(_2\)I with that from HCl, we find some similarities. The low temperature (<315 K) peak and shoulder in Figure 4 vary with exposure in almost the same ways as directly dosed HCl,\(^{56}\) and, at saturation, both have a dominant peak at 220 K with a higher temperature shoulder.

For CICH\(_2\)I, the desorption of HCl sets in at a higher temperature (185–190 K) than CH\(_2\) (170 K), suggesting that C–Cl bonds begin to dissociate at 170 K, producing Cl(a). The latter starts to recombine with surface H atoms to produce gaseous HCl at slightly higher temperature. This is supported by the fact that, when CICH\(_2\)I is dosed with D\(_2\), DCl dominates at 220 K (see section 3.2.1.). Especially for large doses, the H which is reacting, beginning about 180 K, comes mostly from C–H bonds. The amount of CH\(_2\) and HCl desorbing is

\(^{(44)}\) For CH\(_2\)Cl(a) → CH\(_2\)(a) + Cl(a) on Pt(111), we assume each Pt–C covalent bond worth 53 kcal/mol\(^{14}\) and the Cl–Pt(111) bonding energy, D(Cl–Pt) is the same as the desorption energy of atomic Cl. Assuming a first-order kinetics with a prefactor of \(10^3\) s\(^{-1}\) for the desorption of atomic Cl from Pt(111), we estimate a desorption energy of 60 kcal/mol from its desorption peak temperature of \(\sim 950\) K (Figure 16). The value of \(\Delta H\) for the reaction is then equal to \(-[D(\text{Cl–Pt})](66) + 2D(\text{Pt–C}(106) - D(\text{C–Cl}(80) - D(\text{Pt–C}(53))] = -33\) kcal/mol.

background H$_2$ dissociative adsorption (see Figure 5). The high relatively large, so no more than a small fraction comes from background H$_2$ dissociative adsorption (see Figure 5). The high temperature ($\geq 360$ K) HCl peaks in Figure 4 were not observed when HCl was dosed. XPS and HREELS (see below) show evidence that the kinetics are controlled by the dissociation of C$-$H bonds.

Figure 5 shows the H$_2$ TPD spectra. Without dosing ClCH$_2$I, there is a small H$_2$ peak at 370 K, which is due to dissociative adsorption of background H$_2$. Its peak area never exceeds 3% of that obtained by saturating the surface with H$_2$, and, as the ClCH$_2$I exposure increases, its area decreases, disappearing for exposures $\geq 130$ s. Even at the lowest doses, there is another H$_2$ TPD peak at 520 K. A broad H$_2$ peak at 640 K emerges at 50 s exposure. A small H$_2$ peak at 220 K becomes detectable at 75 s exposure; its intensity increases only slightly with ClCH$_2$I exposures shorter than 30 s. H$_2$, HCl, and I are the only desorption products, i.e., each adsorbed ClCH$_2$I molecule decomposes and produces one H atom (or 0.5 H$_2$ molecules), one HCl molecule, and one I atom. The initial linear increase in H$_2$ TPD area (Figure 6) thus yields a ClCH$_2$I accumulation of $8.0 \times 10^{-4}$ ML/s. Stoichiometrically, the initial linear increases in HCl and I TPD areas also correspond to $8.0 \times 10^{-4}$ ML/s. Assuming that the sticking coefficient of ClCH$_2$I at 85 K is constant, independent of coverage, we calculate, based on the measured TPD areas of HCl and I and their initial increases, that at saturation 0.128 ML ClCH$_2$I decomposes and 0.109 ML HCl is produced. Since CH$_3$Cl is the only other C-containing species observed in TPD and no Cl atoms remain on the surface above 500 K, chlorine balance indicates that at saturation 0.019 ML CH$_3$Cl desorbs.

Unlike chlorine, iodine desorbs (not shown) atomically. In agreement with our earlier work, this occurs at high temperatures, peaking between 850 and 925 K, depending on ClCH$_2$I coverages. Compared to chlorine, atomic I is observed, in part, because C$-$I bonds are weaker than C$-$Cl, and H$-$I weaker than H$-$Cl. Therefore, for those adsorbed ClCH$_2$I molecules that undergo C$-$I bond dissociation, some C$-$Cl bonds are preserved and CH$_3$Cl is released as a result of hydrogenation of CH$_2$Cl. While both H(a) + Cl(a) $\rightarrow$ HCl(g) ($\Delta H = 19$ Kcal/mol) and H(a) + I(a) $\rightarrow$ HI(g) ($\Delta H = 44-49$ Kcal/mol) on Pt(111) are endothermic, in all likelihood, the former reaction is activated at much lower temperature, whereas activation of the latter is possible only when surface H is no longer available.

With some reasonable assumptions, we converted the TPD areas, as indicated on the ordinate of Figure 6, to absolute coverages in monolayers [one monolayer (ML) is defined as a surface adspecies/Pt ratio of unity]. Assuming, for dissociative H$_2$ adsorption on Pt(111) at 85 K, that the H/Pt surface ratio is unity when saturation is reached, we can convert the H$_2$ TPD area from ClCH$_2$I/Pt(111) to coverage in ML. When the chemisorbed peak area for parent desorption (175 and 233 K) saturates, we calculate that 0.095 ML H(a) desorbs (as H$_2$). For ClCH$_2$I exposures shorter than 30 s, H$_2$, HCl, and I are the only desorption products, i.e., each adsorbed ClCH$_2$I molecule decomposes and produces one H atom (or 0.5 H$_2$ molecules), one HCl molecule, and one I atom. The initial linear increase in H$_2$ TPD area (Figure 6) thus yields a ClCH$_2$I accumulation of $8.0 \times 10^{-4}$ ML/s. Stoichiometrically, the initial linear increases in HCl and I TPD areas also correspond to $8.0 \times 10^{-4}$ ML/s. Assuming that the sticking coefficient of ClCH$_2$I at 85 K is constant, independent of coverage, we calculate, based on the measured TPD areas of HCl and I and their initial increases, that at saturation 0.128 ML ClCH$_2$I decomposes and 0.109 ML HCl is produced. Since CH$_3$Cl is the only other C-containing species observed in TPD and no Cl atoms remain on the surface above 500 K, chlorine balance indicates that at saturation 0.019 ML CH$_3$Cl desorbs.

(46) The bonding energy is 62 kcal/mol for H$-$Pt(111). We estimate the bonding energy of 53-58 kcal/mol for HCl(g), and 71 kcal/mol for Cl(g) (Wast, R. C. CRC handbook of Chemistry and Physics; CRC Press, Inc.: Boca Raton, FL, 1993). We estimate the bonding energy of 53-58 kcal/mol for H$-$Pt(111) from the desorption peak temperature (850-925 K) of atomic I and by assuming a first-order desorption kinetics with a prefactor of $1 \times 10^{13}$ s$^{-1}$. $\Delta H$ for $"H(a) + Cl(a) \rightarrow HCl(g)"$ on Pt(111) is then $44-49$ kcal/mol. Since the Cl$-$Pt(111) bonding energy is 60 kcal/mol, $\Delta H$ for $"H(a) + Cl(a) \rightarrow HCl(g)"$ on Pt(111) is then 19 kcal/mol.

Carbon balance indicates that at saturation 0.102 ML C is left on the surface. The saturation TPD area of H desorbed at 520 and 650 K in Figure 5 corresponds to an H(\alpha) coverage of 0.088 ML. This indicates that, after the desorption of CH\textsubscript{3}Cl, CH\textsubscript{4}, HCl, and ClCH\textsubscript{2}I has ceased and before the higher temperature (520 and 650 K) H\textsubscript{2} desorption commences (450 K), the surface carbon and hydrogen for a saturation ClCH\textsubscript{2}I dose correspond to a stoichiometry very near that of CH\textsubscript{3}HBEELS (see below) confirms the presence of CH above 370 K.

These results indicate that, for those adsorbed ClCH\textsubscript{2}I molecules undergoing decomposition, complete decomposition to form gaseous H\textsubscript{2} and HCl and surface carbon is a major reaction channel (80\%). The formation of CH\textsubscript{4} (5\%) and CH\textsubscript{3}Cl (15\%) are minor channels. Compared to dosed CH\textsubscript{3}I, the methane yield is much less (0.007 vs 0.08 ML), whereas the C yield is higher (0.102 vs 0.05 ML).\textsuperscript{23} For ClCH\textsubscript{2}I, the relatively weak C–Cl (~80 kcal/mol) bond, compared to C–H (~100 kcal/mol), provides Cl atoms which scavenge surface H atoms, resulting in a hydrogen-deficient situation and, consequently, low yields of CH\textsubscript{4} and CH\textsubscript{3}Cl. When hydrogen is coadsorbed with ClCH\textsubscript{2}I, the yields of CH\textsubscript{4} and CH\textsubscript{3}Cl increase significantly (see section 3.2.).

3.1.2. XPS. To further characterize the dissociation process, the binding energies (BE) of I(3d\textsubscript{5/2}) and Cl(2p) as a function of annealing temperature for a single layer of ClCH\textsubscript{2}I were measured in machine II. The results for monolayer coverage are shown in Figure 7. Similar results were found for a surface dosed with multilayers of ClCH\textsubscript{2}I, except for a dramatic drop of both I(3d\textsubscript{5/2}) and Cl(2p) intensities when the surface was heated to 170 K, a result of multilayer desorption (Figure 1).

At 100 K, XPS shows a symmetric I(3d\textsubscript{5/2}) peak at 620.4 eV and an asymmetric Cl(2p) peak at 199.9 eV (due to overlap of
Figure 7. XPS spectra, taken at 100 K, of I(3d5/2) and Cl(2p) for monolayer ClICH₂I dosed on Pt(111) at 1.0 K and then heated to the indicated temperatures and recooled.

Cl(2p1/2) and Cl(2p3/2). This indicates that ClICH₂I adsorption on Pt(111) at 100 K is mainly nondissociative; otherwise, multiple peaks for I(3d5/2) and Cl(2p) would appear. Upon annealing to any temperature below 150 K, neither I(3d5/2) nor Cl(2p) XPS change. Between 150 and 230 K, both areas decrease, more for Cl(2p) than for I(3d5/2), in harmony with TPD that shows desorption of CH₃Cl and HCl, besides ClICH₂I, in this temperature regime (Figures 1, 2, and 4). After heating to 170 K, there is a low BE I(3d5/2) shoulder (619.2 eV) indicating formation of atomic iodine, I(a). Peak synthesis indicates that 20% of the surface iodine is atomic, I(a), i.e., C–I bonds have broken. A careful comparison of the I(3d5/2) spectra at 100 and 150 K indicates that a small number of C–I bonds dissociate even at 150 K. In contrast, the Cl(2p) position remains unchanged at 170 K. These important observations indicate that the C–I bond breaks first, consistent with TPD that shows a lower onset desorption temperature for CH₃Cl than for CH₄.

When the surface is heated to higher temperatures, the atomic I signal increases at the expense of the signal from the parent molecule. XPS indicates completion of C–I cleavage at 230 K; the I(3d5/2) peak remains unchanged up to 700 K, i.e., constant area, symmetric, and positioned at 619.2 eV. At higher temperatures, I(a) desorbs. Based on TPD (0.13 ML ClICH₂I dissociates) and a comparison of the I(3d5/2) XPS areas at 170 and above 230 K, we calculate that only 0.05 ML of parent ClICH₂I desorbs from a saturated first layer, i.e., dissociation dominates.

Turning to Cl(2p), a small peak appears at about 197.4 eV, indicating C–Cl bond cleavage and formation of Cl(1), when the surface is heated to 200 K. Unlike I(3d5/2), its intensity increases only slightly as the surface is heated to higher temperatures, even though the intensity at 199.9 eV, and thus, the total Cl XPS signal, decreases. Cleavage of additional C–Cl bonds does occur above 200 K, but most of the resulting Cl(a) is promptly removed by reaction with H(a) to form HCl(g). After heating to 285 K, only the 197.4 eV peak remains. No Cl(a) was detected when the surface was heated to 500 K (not shown), consistent with TPD results that show no Cl-containing species desorbing above 500 K for large ClICH₂I doses (Figure 4). The Cl(2p) XPS results indicate that HCl desorbing at 360 and 425 K (Figure 4) is from Cl(a) and confirm that its desorption is reaction-limited, i.e., the cleavage of C–H bonds in surface hydrocarbon fragments controls the HCl(g) formation rate. We note that H(a) does not accumulate above 300 K (see section 3.2.).

3.1.3. HREELS. Guided by TPD and XPS, we used HREELS to identify adsorbed species present at selected temperatures. Figure 8 shows spectra for monolayer and multilayer coverages of ClICH₂I dosed at 100 K and spectra for various annealing temperatures (the annealing temperatures are indicated on each curve, and the spectra were taken after recooling). At 100 K, multilayer ClICH₂I is characterized by

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losses at 540, 740, 820, 1150, 1380, 2970, and 3030 cm\(^{-1}\) and the monolayer at 500, 725, 1140, 1365, 2955, and 3020 cm\(^{-1}\). The assignments, Table 1, match very closely those for liquid CICH\(_2\)I\(^{49}\) confirming nondissociative adsorption of CICH\(_2\)I on Pt(111) at 100 K.

According to TPD and XPS, upon heating to 170 K the multilayer desorbs and some C–I bonds break. The HREELS confirms these processes; the spectrum shows losses at 500, 725, 1140, 1355, 1440, 2900, and 3020 cm\(^{-1}\). The surface should contain both CH\(_2\)Cl(a) and undissociated parent CICH\(_2\)I. Therefore, while assigning the vibrations at 500, 725, 1140, 1355, and 3020 cm\(^{-1}\) to molecular CICH\(_2\)I, we attribute the emerging losses at 1440 and 2900 cm\(^{-1}\) to CH\(_2\)Cl(a). The loss at 1440 cm\(^{-1}\) is assigned to the scissor mode and that at 2900 cm\(^{-1}\) to the C–H stretching of CH\(_2\) in CH\(_2\)Cl(a). The latter is softened, compared to the parent, due to stronger coupling with the substrate. Similar observations have been made for CH\(_3\)I and CH\(_3\) adsorbed on Pt(111):\(^{14}\) the symmetric C–H stretching at 2970 cm\(^{-1}\) for CH\(_3\)I(a) moves to 2925 cm\(^{-1}\) for CH\(_3\)I(a).

As expected, losses attributed to parent CICH\(_2\)I decrease when the surface is heated to 200 K, a result of molecular desorption and further dissociation. The latter leads to little change at 1440 and 2900 cm\(^{-1}\) because, during heating to 200 K, cleavage of additional C–I bonds is accompanied by hydrogenation and dissociation of CH\(_2\)Cl(a) to form gas phase CH\(_3\)Cl(g) and CH\(_3\)I(g) along with adsorbed CH\(_2\)(a) and Cl(a). Any CH\(_2\)(a) will contribute intensity to the 1440 and 2900 cm\(^{-1}\) loss regions. These gains and losses tend to compensate, resulting in little intensity change. A new loss, assigned to Pt–Cl stretching, emerges at 300 cm\(^{-1}\),\(^{45,55}\) Formation of Cl(a) at these temperatures is supported by the XPS data. Parenthetically, the

Pt–I stretching frequency is probably too low to be resolved from the elastic peak.

Consistent with TPD and XPS, the HREELS spectra taken after heating to 230 and 260 K reflect removal of most and all the parent, respectively. At 260 K, the losses at 480, 775, and 2940 cm⁻¹ are attributed to CH(a), i.e., Pt–C stretching, C–H bending, and C–H stretching, respectively. The peak at 1440 cm⁻¹ and the shoulder at 2880 cm⁻¹ are attributed to a small amount of CH₂(a) (see analysis below). No noticeable change in HREELS occurs when the surface is heated from 260 to 320 K, consistent with TPD that shows little desorption in this region.

When the surface is heated to 370 K, the Pt–Cl loss becomes significantly weaker, the 1440 cm⁻¹ peak and the shoulder at 2880 cm⁻¹ disappear. The losses attributed to CH(a) intensify slightly and the loss at 2940 cm⁻¹ sharpens. These changes correlate with the TPD; HCl and a small amount of CH₄ desorb. We propose that, at 370 K, the surface retains CH(a), I(a), and a small quantity of Cl(a). The likely reactions at 355–360 K include 3CH₂(a) → 2CH(a) + CH₄(g) and CH₂(a) + Cl(a) → CH(a) + HCl(g).

Heating to 450 K eliminates the Pt–Cl stretch, consistent with HCl desorption at 415 K. At the same time, CH(a) intensities decrease and new losses emerge at 830 and 3035 cm⁻¹. Between 450 and 540 K, CH(a) fragments dehydrogenate further, releasing H₂ at 520 K (Figure 5) and forming the species which give rise to the 830 and 3035 cm⁻¹ signals. Tentatively, we assign them to η²-CCH(a) (see below). They dominate after heating to 540 K but disappear by 800 K along with all other losses.

Before ending this section, we return to the losses at 1440 and 2880 cm⁻¹. As shown in Figure 8, after the surface is heated from 320 to 370 K, the HREELS peak in the C–H stretching region narrows and becomes symmetric and the loss at 1440 cm⁻¹ disappears; the spectrum can be assigned to a single species, CH(a). To reduce the complexity of the spectra at 260 and 320 K, we subtracted, from each, a normalized version of the 370 K spectrum. The 775 cm⁻¹ peaks were all normalized to unity, and the resulting spectra are shown in Figure 9. The difference spectra, though noisy, show three distinct peaks (300, 1440 and 2880 cm⁻¹). There may also be a peak at 2990 cm⁻¹. The 300 cm⁻¹ peak is due to Pt–Cl stretching. The difference spectra are reasonably assigned to CH₂(a) with C₂v symmetry (Chart 1). Based on the dipole selection rule, we expect three loss modes. Symmetric C–H stretching (2880 cm⁻¹), CH₂ scissoring (1440 cm⁻¹), and Pt–C stretching (probably too weak to be observed). We will discuss this assignment in section 4.

3.1.4. POTPD. To monitor the cleavage of C–H bonds, we used predosed oxygen TPD (POTPD),4¹ a thermal desorption and reaction technique based on scavenging H(a) by small amounts of preadsorbed O(a), formed from O₂. Provided the reaction temperature is above the normal water desorption temperature, the resulting water desorbs promptly and is easily detected. When hydrocarbon fragments dissociate and supply H, this water desorption monitors the C–H bond cleavage and, thus, characterizes the kinetics of dehydrogenation of hydrocarbon fragments on Pt(111).4¹

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The upper panel in Figure 10 shows the H$_2$O TPD for a multilayer CICH$_2$I dosed on Pt(111) covered with 0.01 ML of O(a). Under these conditions, the only oxidation product is H$_2$O. Other products are distributed as when O(a) is absent, except that the TPD areas of H$_2$, CH$_4$, HCl, and CH$_3$Cl are slightly smaller. The H$_2$O TPD shows a peak at 215 K with an onset of about 170 K (dashed curve). To confirm that the H$_2$O desorption is rate-limited by the C-H bond cleavage, we exposed 0.01 ML $^{18}$O$_2$ first to 0.3 L D$_2$ and then to CICH$_2$I for 300 s at 90 K. In this case, H$_2$O, HDO, and D$_2$O are all observed, and they have an onset of about 170 K (lower panel of Figure 10). However, the peak temperatures are measurably and reproducibly different—H$_2$O (215 K) > HDO (211 K) > D$_2$O (208 K). Above 208 K, as the D$_2$O desorption rate decreases due to the depletion of D(a), the rate of H supply, from the C-H bond dissociation, for forming H$_2$O continues to increase, resulting in the observed order. Since H(a) from the background contributes particularly in the low temperature portion of the H$_2$O TPD, the observed onset temperature for H$_2$O desorption is not a true measure of the onset for C-H bond dissociation. To account for this background effect, we took the following approximations. First, because isotope effects do not alter the onset temperature significantly, we neglected them in Figure 10. Under our experimental conditions, the D(a) coverage for a 0.3 L exposure of D$_2$ is 3.5 times the H(a) coverage adsorbed from background. Then, for the reaction of O(a) + 2H(a) [or 2D(a)] → H$_2$O(g) [or D$_2$O(g)], we subtracted the intensity of (D$_2$O + 0.5HDO)/3.5 from the dashed curve to eliminate the contribution of H$_2$O formed from background H(a) to the observed H$_2$O desorption intensity. The resulting spectrum (solid curve in the upper panel) shows a peak at 215 K with an onset of about 180 K, which we take as the onset of C-H bond dissociation. Thus, we conclude, consistent with the TPD of CH$_4$ and CH$_2$Cl, that C-H bond breaking sets in at 180 K and becomes quite rapid above 200 K. This is in agreement with the onset temperature of dehydrogenation of CD$_2$ derived from CD$_3$I$_2$, on Pt(111) where the effect of background hydrogen was eliminated.$^{31}$

3.2. CICH$_2$I on D/Pt(111). To gain further insight, we examined cases in which both low and high coverages of atomic D were coadsorbed with slightly more than one layer of CICH$_2$I at 90 K. In TPD, we observed deuteriation and H-D exchange products, i.e., $d$-labeled methyl chloride, hydrogen chloride, and methane.

Figure 11 compares the parent CICH$_2$I desorption with and without coadsorbed D. While the 157 (multilayer) and 176 K peaks remain unchanged when D is coadsorbed, the 233 K peak decreases and almost disappears when the coverage of D(a) is 0.5 ML. There is also a new parent peak (197 K at $\theta_D = 0.15$ ML), which intensifies and shifts to slightly lower temperature with increasing $\theta_D$. Clearly, surface D lowers the desorption activation energy and reduces the dissociation of CICH$_2$I. Comparing the amounts of atomic I that desorb, we calculate that 0.128, 0.12, 0.102, and 0.051 ML CICH$_2$I dissociates when 0.00, 0.15, 0.5, and 1.0 ML D(a), respectively, is present (Table 2).

Figure 12 shows the TPD spectra of hydrogen isotopes (panel A), methane (panel B), hydrogen chloride (panel C), and methyl chloride (panel D) for a multilayer CICH$_2$I coadsorbed with 0.15 ML D. For dihydrogen in the low temperature regime, there is a peak at 226 K for D$_2$, 230 K for HD, and 233 K for H$_2$. Desorption at these temperatures, the sharpness of the peaks, and the sequence D$_2$ < HD < H$_2$ are all consistent with desorption controlled by C-H cleavage, with an onset near 180 K, as for POTPD. In the high temperature regime, there are two peaks for H$_2$ and HD but no signal for D$_2$; HD peaks are much weaker than H$_2$. These facts indicate some, but very little, H-D exchange to form C-D bonds.

For methane (panel B), there is a peak at about 198 K for CH$_4$, CH$_3$D, CH$_2$D$_2$, CHD$_3$, and CD$_4$; CH$_3$D and CH$_2$D$_2$ are the strongest and both have onsets at about 170 K. Formation of CHD$_3$ and CD$_4$, requiring isotope exchange between D(a) and H in CH$_2$(a), is not surprising because exchange is kinetically facile on Pt(111).$^{25}$ There is also a peak at 226 K for CH$_3$D$_2$, a peak at 230 K for CH$_4$D, and a peak at 233 K for CH$_4$; the CH$_4$D peak is the most intense. For CH$_4$ and CH$_3$D there are relatively intense peaks at 355 K, but CH$_2$D$_2$ is barely detectable.

For hydrogen chloride (Figure 12C), DCI peaks at 220 K and HCl shows a strong peak at 225 K and two small peaks at 360 and 420 K. As in the absence of D(a), desorption of atomic Cl was not found. Compared to the clean surface (Figure 4), the high temperature peaks, 360 and 420 K, are much weaker when D is coadsorbed.

For methyl chloride (Figure 12D), there are two peaks, 190 and 220 K, for CH$_3$Cl and CH$_2$DCI but not for CHD$_2$Cl. It is interesting that no more than one D atom is incorporated into methyl chloride, while, in small amounts, fully deuterated methane (CD$_4$) is detected. This indicates that, unlike methane formation, no H-D exchange is involved in methyl chloride formation. We conclude that methyl chloride arises exclusively from the hydrogenation of CH$_2$Cl(a) and that its concentration drops to zero at about 240 K. It is also interesting that the CH$_3$DCI/CH$_2$Cl ratio is higher at 190 K than at 220 K. We understand this change as follows. At 190 K, the dehydrogenation is relatively slow, and the concentration of D exceeds H; thus, hydrogenation of CH$_2$Cl by D(a) dominates. At 220 K, dehydrogenation is rapid, much of the D is already consumed, and the resulting H atoms participate in hydrogenation of CH$_2$Cl, increasing the relative CH$_3$Cl yield.

Figure 13 shows the TPD results for CICH$_2$I adsorbed on a higher coverage, 0.5 ML, of D(a). As expected, the relative concentration of D in the TPD products is higher than for $\theta_D =$
Figure 10. Upper panel: dashed curve—H₂O TPD spectrum for a multilayer coverage of CICl₂I dosed on 0.01 ML ¹⁸O/Pt(111); solid curve—dashed curve minus the intensity of [(D₂O + 0.5HDO)/3.5] from the lower panel (see text for details). Lower panel: H₂O, HDO, and D₂O TPD spectra for a multilayer coverage of CICl₂I on 0.01 ¹⁸O pre-dosed with 0.3 L D₂ at 90 K. The H₂O curve has been corrected for cracking of D₂O and HDO at 18 amu. The heating rate was 6 K/s.

0.15 ML. The lowest peak temperatures for dihydrogen desorption are slightly higher but have the same order, i.e., H₂ > HD > D₂ (Figure 13A). For methane (Figure 13B), there is no CH₄ peak at about 194 K and no peaks at 355 K. Instead, there is a new peak at 272 K for CH₃, CH₃D, and CH₂D₂. This is likely the result of hydrogenation of a methyl intermediate, CH₃D₃-x, because for CICl₂I coadsorbed with submonolayer CD₃ᵢ, there was a distinct peak at 275 K for CD₃H (not shown). For hydrogen chloride, there are no peaks at 360 and 420 K. For methyl chloride (Figure 13D), there are no qualitative differences compared to θ₀ = 0.15 ML case.

The isotope distributions in methane, methyl chloride, and hydrogen chloride are summarized in Figures 14 and 15. For methane, the overall isotope distribution shifts to favor more D atoms in each molecule as θ₀ increases. Although CHD₃ and CD₄ are detected for both low and high θ₀'s, their yields are very low as compared to CH₃D and CH₂D₂, indicating that the isotope exchange between D and H in CH₂ is not strongly competitive with hydrogenation and dehydrogenation of CH₂. The relative yields of CHD₃ and CD₄, compared to total methane (see Table 2), increase with θ₀. The ratios of DCI/HCl and CH₂DCI/CH₃Cl increase monotonically with increasing θ₀ (Figure 15).

The total yields of methane, methyl chloride, hydrogen chloride, and iodine in TPD and surface carbon as a function of θ₀ are shown in Table 2. The iodine yield decreases monotonically with increasing θ₀. For those adsorbed CICl₂I molecules that dissociate, the fraction of complete dissociation to form surface carbon decreases monotonically from 80% on D-free surface to 27% on 1 ML D/Pt(111). Correspondingly,
the relative yields of methane and methyl chloride increase monotonically with $\theta_D$. All these indicate that coadsorbed D(a) blocks the dissociation of ClCH$_2$I, suppresses the dehydrogenation of CH$_2$, and enhances hydrogenation of CH$_2$Cl and CH$_2$.

We have also taken the I(3d$_{5/2}$) XPS, for coadsorbed ClCH$_2$I and D, as a function of annealing temperature (results not shown). As on a D-free surface, the C–I bond starts to dissociate at 150 K, consistent with the onset temperature of CH$_2$DCI desorption. For the same exposure of ClCH$_2$I and increasing $\theta_D$, XPS indicates less and less atomic iodine after heating to 300 K, a result in agreement with the iodine TPD.

Even though D-for-H exchange reaction is detected in hydrogen and methane TPD, no C–D stretching signal was observed in HREELS between 100 and 700 K. A comparison of HD and H$_2$ TPD areas in Figure 12 and 13 indicates that the concentration of CD(a) is no more than 5% of that of CH(a) and probably lies below the detection limit of HREELS.

### 3.3. ClCH$_2$I Coadsorbed with Atomic Oxygen

Because the oxidation of C$_1$ hydrocarbon fragments on metal surfaces is fundamentally related to the mechanism of catalytic oxidation of methane to form methanol, and because the catalytic oxidation of halogenated hydrocarbon wastes is environmentally interesting, we have also investigated the thermal reaction of ClCH$_2$I with coverages of O(a) that exceed those used in POTPD. Figure 16 shows the TPD results for a multilayer dose of ClCH$_2$I on 0.25 ML $^{180}$O(a). For parent ClCH$_2$I, there is a new desorption peak at 305 K, in addition to the two other peaks that are found on O-free surfaces. Surface iodine desorbs atomically above 700 K with a peak at about 855 K. H$_2$ TPD is barely detectable. Methane and methyl chloride are still produced at 230 and 215 K, respectively, but their intensities are much lower than on an O-free surface. HCl shows several peaks—230, 270, 305, 350, and 460 K.

![Figure 11. TPD spectra of ClCH$_2$I for a multilayer exposure of ClCH$_2$I on clean and D-covered Pt(111). The D coverage (ML) is indicated on each curve.](image1)

![Figure 12. TPD spectra of dihydrogen (panel A), methane (panel B), hydrogen chloride (panel C), and methyl chloride (panel D) for a multilayer coverage of ClCH$_2$I on 0.15 ML D.](image2)
Figure 13. TPD spectra of dihydrogen (panel A), methane (panel B), hydrogen chloride (panel C), and methyl chloride (panel D) for a multilayer coverage of CICH$_2$I on 0.5 ML D.

Figure 14. Isotope distributions in methane produced by heating a multilayer dose of CICH$_2$I over various amounts of D at 85 K.

Products not found on O-free surfaces are H$_2$O$^{18}$, C$^{18}$O, CH$_3$O$^{18}$ (formaldehyde), CI, C$^{18}$O$_2$, and CH$_2$Cl$_2$. For the 30 amu ion signal, largely C$^{18}$O$^+$, contributions from the fragmentation of C$^{18}$O$_2$ and CH$_2$$^{18}$O have been subtracted. And, for C$^{18}$O$_2$, the contribution of CHCl$^+$ (m/e = 48) from the fragmentation of CICH$_2$I and CH$_2$Cl$_2$ has been subtracted.
Table 1. Assignments of Vibrational Spectra (cm⁻¹) of CICH₂I

<table>
<thead>
<tr>
<th>mode</th>
<th>multilayer CICH₂I/Pt(111)</th>
<th>monolayer CICH₂I/Pt(111)</th>
<th>CICH₂I (52)</th>
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</thead>
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<tr>
<td>ν(CH₂)</td>
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<td>3030</td>
<td>3048</td>
</tr>
<tr>
<td>ν(CH)</td>
<td>2955</td>
<td>2970</td>
<td>2979</td>
</tr>
<tr>
<td>δ(CH₂)</td>
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<td>1380</td>
<td>1392</td>
</tr>
<tr>
<td>δ(CH₃)</td>
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<td>1150</td>
<td>1183</td>
</tr>
<tr>
<td>ν(Γ)</td>
<td>not resolved</td>
<td>820</td>
<td>801</td>
</tr>
<tr>
<td>ν(C–Cl)</td>
<td>725</td>
<td>740</td>
<td>718</td>
</tr>
<tr>
<td>ν(C–I)</td>
<td>500</td>
<td>540</td>
<td>527</td>
</tr>
</tbody>
</table>

*νₓ, asymmetric stretching; νₛ, symmetric stretching; δ, deformation or scission; ω, wagging; τ, twisting; γ, rocking.

This is the first time, on Pt(111), that formaldehyde has been reported from the UHV reaction between a CH₃ precursor and atomic O, in the presence of coadsorbed halogens. Whereas in the absence of O(a), atomic Cl desorption is not observed, it clearly desorbs at about 950 K in the presence of O(a). This can be easily understood; O(a) scavenges most H atoms to form H₂O, leaving insufficient H to form HCl. For the same reason, H₂ is not observed in TPD.

The detailed TPD results for a multilayer exposure of CICH₂I, preadsorbed with different coverages of O(a), are shown in Figure 17, and the TPD areas of the reaction products versus θ₀ are summarized in Figure 18. With increasing θ₀, all the hydrogenation products decrease, while Cl, CH₂Cl₂ and the oxidation products increase. Generally, these changes are the result of very effective consumption of H(a) by O(a). For parent CICH₂I (panel A), the peak intensity at 235 K decreases with increasing θ₀, but the high temperature cutoff increases. At θ₀ = 0.12 ML, there is a shoulder at 305 K which intensifies and becomes a distinct peak at θ₀ ≥ 0.19 ML. For CH₄ (panel B), the shoulder at 200 K and small peak at 355 K found on O-free surfaces both disappear at θ₀ = 0.035 ML. For CH₃Cl (panel C), the intensity drops, but the shape and position change very little. For HCl (panel D), a new peak appears at 305 K for θ₀ = 0.12 ML, and its intensity increases with the coverage of oxygen. The highest temperature HCl peak (415 K) first intensifies and then diminishes with increasing θ₀; the peak temperature, however, increases monotonically to 460 K at θ₀ = 0.25 ML. All the H₂ peaks decrease with increasing θ₀ (panel E).

We now turn to the products that increase with θ₀. The number and strength of the H₂O (panel 17 F) peaks varies with θ₀. One strong peak at 225 K sets in at low coverage, this is the first time, on Pt(111), that formaldehyde has been reported from the UHV reaction between a CH₃ precursor and atomic O, in the presence of coadsorbed halogens. Whereas in the absence of O(a), atomic Cl desorption is not observed, it clearly desorbs at about 950 K in the presence of O(a). This can be easily understood; O(a) scavenges most H atoms to form H₂O, leaving insufficient H to form HCl. For the same reason, H₂ is not observed in TPD.
maximizes ($\theta_0 = 0.12$ ML), and then decreases. Several higher temperature $H_2O$ peaks, which we associate with dissociation processes that produce $H(a)$, emerge at high $\theta_0 = 0.35$ K appears at $\theta_0 = 0.06$ ML, a 350 K peak at $\theta_0 = 0.035$ ML, and a 380–410 K peak at $\theta_0 = 0.12$ ML. While the 350 K peak appears to approach saturation, the other two peaks increase monotonically. $CH_2Cl_2$ (panel G) is first detected at $\theta_0 = 0.035$ ML; it intensifies with increasing $\theta_0$. $CH_3O$ (panel H) is also first detected at $\theta_0 = 0.035$ ML. The lowest temperature peak at 175 K saturates at $\theta_0 = 0.12$ ML, while a second peak (280 K) emerges at $\theta_0 = 0.06$ ML and grows monotonically. Likewise, $CO_2$ (panel I) desorption is first detected at $\theta_0 = 0.035$ ML (peaks at 305 and 360 K). For $\theta_0 \geq 0.19$ ML, an additional peak at 425 K emerges. Ignoring background desorption peaked at 400 K, there is only one CO peak at 445 K (panel J); its area has a local maximum at $\theta_0 = 0.12$ ML.

As shown in Figure 18, the iodine TPD area decreases slowly with increasing $\theta_0$; adding $\theta_0 = 0.25$ ML of O(a) reduces the dissociation by 20%.

XPS data were also taken in the presence of O(a) (Figure 19). Slightly more than one layer of ClCH$_2$I was added to 0.25 ML O(a) at 100 K. The BEs, reflecting nondissociative adsorption, are 620.4 eV for I(3d$_{5/2}$) and 199.9 eV for Cl(2p), just as on the O-free surface (Figure 7). Upon annealing briefly to 170 K, both I(3d$_{5/2}$) and Cl(2p) weaken due to multilayer ClCH$_2$I desorption. As the annealing temperature increases, the Cl(2p) peak position remains unchanged up to 210 K, while I(3d$_{5/2}$) broadens slightly toward lower BE even at 170 K, as on the O-free surface, C–I bonds break more readily than C–Cl.

Above 310 K, the I(3d$_{5/2}$) spectra no longer change. Between 210 and 250 K, C–Cl cleavage is evidenced by growth of a peak at 197.3 eV. Its intensity does not increase much, if at all, at higher temperature; even though the surface concentration of Cl–C bonds drops dramatically, most of the Cl is carried off in desorbing products. Some 199.9 eV Cl(2p) signal remains at 290 K, but not at 320 K; i.e., C–Cl bonds are lost in this interval. The desorption of CH$_2$O, H$_2$O, and CH$_4$ (Figure 16) below 210 K indicates the availability of H(a) and CH$_2$O(a). However, based on the absence of detectable XPS intensity at
Figure 17. TPD spectra of ClCH$_2$I (A), CH$_4$ (B), CH$_3$Cl (C), HCl (D), H$_2$ (F), H$_2$O (G), CH$_2$Cl (H), CH$_3$NO (I), C$_4$H$_6$O$_2$ (J), and C$_3$H$_5$O (K) for multilayer ClCH$_2$I coadsorbed with various amounts of atomic oxygen, $\theta_O$=0, 0.015, 0.035, 0.06, 0.12, 0.19, and 0.25 ML—on Pt(111) at 85 K. The heating rate was 6 K/s.

197.3 eV, the dissociation of C−Cl to form Cl(a) is slow below 210 K (see HREELS data below).

Figure 20 shows the HREELS results for about two layers of ClCH$_2$I adsorbed on 0.25 ML O(a) at 100 K and then heated to different temperatures. For O alone on Pt(111), HREELS shows a peak at 460 cm$^{-1}$, corresponding to Pt-O stretching, in
agreement with literature.\textsuperscript{53a} After adsorbing ClCH\textsubscript{2}I, the 100 K spectrum is identical to that on the clean surface except for the shoulder at 460 cm\textsuperscript{-1} (due to Pt-O stretching). As when O(a) is absent, heating to 170 K shows an additional peak at 1440 cm\textsuperscript{-1} and a shoulder at 2855 cm\textsuperscript{-1}. When the surface is further heated to 210 K, no other significant changes occur except for the emergence of a weak peak at 300 cm\textsuperscript{-1} due to Pt–Cl stretching. As expected, at 250 and 280 K, the Cl(a) intensity is stronger, while the losses associated with ClCH\textsubscript{2}I are weaker. There are also changes in the C=H stretching region; a peak at 2940 cm\textsuperscript{-1} emerges. Heating to 320 K eliminates all the loss features due to molecular ClCH\textsubscript{2}I, consistent with TPD (Figure 16), increases the intensity at 2940 cm\textsuperscript{-1} and decreases the intensity at 460 cm\textsuperscript{-1}. The other losses observed at 320 K are at 300, 460, 770, 1440, and 2855 cm\textsuperscript{-1} (shoulder). Heating at 370 K eliminates the weak losses at 1440 and 2855 cm\textsuperscript{-1}, reduces the loss intensities at 300, 460, 770, and 2940 cm\textsuperscript{-1}, and introduces two new losses at 850 and 3050 cm\textsuperscript{-1}. At 500 K, a weak Pt–Cl stretching signal at 300 cm\textsuperscript{-1} is detected; all the other loss features disappear, in harmony with TPD (Figure 16) that shows desorption of only Cl and I above 500 K [I(a) has never been detected with HREELS in this study].

An important point can be made from the HREELS data, i.e., there is no loss peak that can be assigned to ν(C–O) (1000–1400 cm\textsuperscript{-1}), ν(C=O) (1600–2200 cm\textsuperscript{-1}), or ν(O–H) (3200–3600 cm\textsuperscript{-1}). This indicates that possible oxygen-containing intermediates which have dipole-active C–O and O–H stretching modes, such as H\textsubscript{2}O, OH, CO, and CH\textsubscript{2}O (formate) \textsuperscript{53b–d}, do not accumulate on the surface from the reaction of ClCH\textsubscript{2}I with O(a). The accumulation of another intermediate, di-σ-bonded –OCH\textsubscript{2}–, which we propose is a primary reaction intermediate (see section 4.3.), cannot be ruled out based on the HREELS data because its C–O bond is parallel to the surface and, thus, dipole-inactive. However, its accumulation is ruled out by the fact that dosed CH\textsubscript{2}O decomposes to CO and H on Pt(111) even at 105.\textsuperscript{56} These facts indicate that the desorption kinetics of all the oxidation products are reaction limited.

4. Discussion

4.1. Reactions of ClCH\textsubscript{2}I on Clean Pt(111). We turn now to a discussion of the reaction pathways followed by ClCH\textsubscript{2}I adsorption on Pt(111). For monolayer ClCH\textsubscript{2}I, Scheme 1 provides a summary. Moving from top to bottom, the temperature increases from 85 to 800 K, as indicated along the left-hand side. For each temperature regime, proposed surface species are listed in the ovals, TPD products in the rectangles, and reaction events on the horizontal lines.

Beginning at the top (85 K), both XPS and HREELS results provide solid evidence that molecular adsorption dominates throughout the monolayer range. In TPD, however, parent
Figure 19. Cl(2p) and I(3d_{5/2}) XPS for a multilayer ClCHI dosed onto 0.25 ML of atomic oxygen and heated to the indicated temperatures.

desorption appears only for coverages above half-monolayer, with peaks at 175 and 233 K. For lower coverages, TPD, with and without coadsorbed D(a), reflects dissociation during heating; adding D(a) enhances the amount of parent desorption and lowers the desorption temperature. Starting at 150 K, there is XPS evidence for I(a), but not Cl(a), i.e., activated C–I cleavage occurs leaving products with the C–Cl bond intact. Methyl chloride desorption at 190 K, especially CH₂DCI(g) which dominates when D(a) is preadsorbed, supports CH₂Cl-(a) as an important dissociation product. C-Cl dissociation is also activated but begins at higher T (170 K) and is signaled by the onset of CH₄ desorption. Accumulation of some Cl(a) is confirmed by XPS and HREELS data taken after heating to 200–230 K. Methane desorption is attributed to hydrogenation of CH₃(a). This conclusion is supported by isotope tracing summarized in Figures 12 and 13; when D(a) is dominant, CH₂D and CH₂D₂ overwhelmingly dominate on the leading edges of the methane TPD, i.e., at ~200 K. POTPD, scavenging of H(a) by tiny amounts of O(a), confirms that H, attributed to C–H cleavage, starts becoming available at 180 K, presumably producing CH(a) and H(a). At 190 K, the reactions H(a) + Cl(a) → HCl(g) and 2H(a) → H₂(g) become activated. All these hydrogenation processes become rapid above 200 K.

Between 150 and 200 K, several kinetically competitive pathways are important. Among them are the following:

1. C–I bond dissociation competing with parent molecule desorption
2. Hydrogenation of CH₂Cl competing with Cl–C bond dissociation
3. Hydrogenation competing with dehydrogenation of CH₂-(a)

With regard to the second of these, hydrogenation has a lower activation energy (occurs at a lower temperature). Above 210 K, however, the C–Cl dissociation rate dominates. Note, in Figure 2, that the CH₂Cl desorption drops steeply above 210 K even though more CICH₂Cl molecules dissociate (see Figure 7) and many C–H bonds break (as evidenced by intense CH₄, CH₂Cl, and HCl desorption) to provide H. Apparently, above 210 K, once the C–I bond breaks, the activation requirement for C–Cl cleavage is immediately realized so that hydrogenation to form CH₃Cl can no longer compete.

Between 150 and 200 K, a number of important intermediates have been identified. I(a) and Cl(a) were identified by XPS. Cl(a) was also confirmed by the appearance of a 300 cm⁻¹ band in HREELS. Other emerging HREELS losses (1440 and 2900 cm⁻¹) at 170 K are taken as evidence for CICH₂Cl, a hydrogenation product of CICH₂I, and with XPS that shows extensive cleavage of C–I, but not C–Cl, bonds. One expects other losses due to CICH₂, e.g., C–Cl and C–Pt stretching but these very likely are buried under the intense features associated with remaining parent CICH₂I.

After heating to 260 K, there is HREELS evidence for the accumulation of CH(a) fragments. Besides CH(a), some CH₂-(a) fragments also survive. Tables 3 and 4 compare the vibrational frequencies assigned to CH₃(a) and CH₂(a), respectively, on Pt(111) and other surfaces. CH₃(a) is not considered; it is excluded by the absence of an expected intense loss at 1165
cm$^{-1}$. While the wagging, twisting, and rocking modes of CH$_2$(a) have been observed on Ru(001) and Fe(110), they are not found in the present case, perhaps due to symmetry ($C_3v$) considerations (see Chart 1). If the noisy peak at 2990 cm$^{-1}$ in Figure 9 is a real feature, then it has to be assigned to the asymmetrical CH$_2$ stretching, which might result from the impact scattering of the C$_2$ CH$_2$(a). The HREELS features at 2940, 775, and 480 cm$^{-1}$ are typical of CH(a) whose vibrational characteristics are very well documented (Table 4).

Turning to the structure of CH(a), the intense C–H stretching at 2940 cm$^{-1}$ for CH(a) suggests sp$^3$ hybridization at the carbon and, sensibly, that CH is bound at threefold Pt sites with the C–H bond perpendicular to the surface (Chart 2). In this orientation, the C–H stretching mode is normal to the surface and, thus, dipole-active, while the C–H bending mode is parallel to the surface normal and dipole-inactive. In this geometry, the relatively weak C–H bending (775 cm$^{-1}$, Figure 8), compared to the intense C–H stretching, would be attributed to impact scattering. Similar observations and interpretations have been reported for CH on Ru(001) and Ni(111). Alternatively, the C–H bond may be tilted away from the surface normal. Although such an orientation would allow both the C–H bending and stretching to be dipole-active, it is not favored from an energetic point of view. In Chart 2, the three

Scheme 1

Monolayer ClCH$_2$I on Pt(111)

**Surface Species**

- Adsorption at 85 K

- C-I bond activated at ~150 K

- C-Cl bond activated at ~170 K, hydrogenation of CH$_2$Cl and CH$_2$

**TPD Products**

- Negligible desorption

- ClCH$_2$I (175 K)

- CH$_3$Cl (190 K)

- CH$_4$ (200 K)

- ClCH$_2$I (175 K)

- CH$_3$Cl (190 K)

- CH$_4$ (200 K)

- H$_2$ (220 K)

- CH$_3$Cl (210 K)

- CH$_4$ (220 K)

- HCl (220 K)

- ClCH$_2$I (233 K)

**Reaction 2CH + Cl -> CCH + HCl**

- Activated HCl (360 K)

**Reaction 2CH + Cl -> CCH + HCl**

- Activated HCl (360 K)

**Reaction 4CH + CH$_4$ + HCl**

- Activated HCl (360 K)

**Reaction 4CH + Cl -> CCH + HCl**

- Activated HCl (360 K)

**Reaction 4CH + Cl -> CCH + HCl**

- Activated HCl (360 K)

**I > CH > Cl > CH$_2$**

**I > CH > Cl**

**I > CH > CCH**

**I > CCH**

**I and C$_n$ (n=2)**

**Table 3. Vibrational Frequencies (cm$^{-1}$) Assigned to CH$_2$ Species**

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<td>3050</td>
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<td>943</td>
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<tr>
<td>$\omega$(CH$_3$)</td>
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<td>1140</td>
<td>1140</td>
<td>961</td>
<td>943</td>
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<tr>
<td>$\gamma$(CH$_3$)</td>
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<td>900</td>
<td>900</td>
<td>869</td>
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<td>869</td>
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<tr>
<td>$\phi$(CH$_3$)</td>
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$^a$ This work. $^b$ Reference 34. $^c$ Reference 36. $^d$ Reference 33. $^e$ Reference 35. $^f$ Reference 38. $^g$ Reference 7. $^h$ (μ$_2$-H)$_2$Os$_2$(CO)$_2$(μ$_2$-CH$_2$), ref 54.

The $\nu_{\text{as}}$(CH) and $\nu_{\text{s}}$(CH) vibrations of CH$_2$Cl and CH$_2$Cl$_2$ are strong and sharp, indicating a strong interaction between the CH$_2$ group and the underlying metal surface. The $\delta$(CH$_3$) vibration of CH$_3$Cl is also strong, indicating a strong interaction between the CH$_3$ group and the underlying metal surface. The $\omega$(CH$_3$) vibration of CH$_3$Cl is weak, indicating a weak interaction between the CH$_3$ group and the underlying metal surface. The $\gamma$(CH$_3$) vibration of CH$_3$Cl is strong, indicating a strong interaction between the CH$_3$ group and the underlying metal surface. The $\phi$(CH$_3$) vibration of CH$_3$Cl is weak, indicating a weak interaction between the CH$_3$ group and the underlying metal surface. The $\nu_{\text{as}}$(MC) and $\nu_{\text{s}}$(MC) vibrations of MC are strong, indicating a strong interaction between the MC group and the underlying metal surface. The $\nu_{\text{as}}$(MC) and $\nu_{\text{s}}$(MC) vibrations of MC are weak, indicating a weak interaction between the MC group and the underlying metal surface.
the C–H bond inclined away from the surface normal (see Chart 3). An alternative, involving \( \eta^2 \)–CCH(a), should also be considered (see discussion below).

The CH₂(a) that remains at 260 K disappears by 370 K (HREELS evidence). Desorption of CH₂ and HCl in the range 355–360 K points to further dehydrogenation (i.e., CH₂(a) \( \rightarrow \) CH(a) + H(a)) and hydrogenation (i.e., CH₂(a) + 2H(a) \( \rightarrow \) CH₃(g) and H(a) + C(a) \( \rightarrow \) HCl(g)) competing and both removing CH₂(a). Based on relative TPD areas in the 355 K temperature range, we estimate that 0.021 ML of CH₂(a) is present at 260 K. It is not clear why this amount survives, while the majority (0.088 ML, refer to Table 2) reacts at lower temperature. While coadsorbed halogens may play some role, we note that for CH₂ Le., no halogens, on Pt(111), CH desorption also extended to high temperature (400 K). Thus, other factors, e.g., local adsorbate structural organization, may be important.

(64) Ceyer, S. T.; Langmuir 1990, 6, 82.

Continuing with scheme 1, at 400 K, the species remaining on the surface are I(a), Cl(a), and CH(a). The Cl(a) desorbs as HCl at 415 K (Figure 4), the hydrogen atoms coming from CH(a). The attenuation of CH(a) vibrational modes supports this proposal. Stoichiometric balance also points to CH(a); the H₂ desorbed above 400 K, for 2200 s exposures, corresponds to 0.088 ML H(a). The coverage of C(a) retained at 1000 K is 0.102 ML. The difference between C(a) and H(a), 0.014 ML, nearly equals the 0.019 ML of HCl that desorbs at 415 K. The emergence, at 450 K, of new loss features (830 and 3035 cm⁻¹), indicates that HCl formation is accompanied by a reaction other than conversion of CH(a) to C(a). We propose a reaction producing HCl(g) + CCH(a). More CCH(a) appears at 540 K, but at 640 K it dehydrogenates, leaving carbon on the surface and yielding a broad H₂ peak centered at 640 K.

Turning to the surface species responsible for the vibrational peaks at 830 and 3035 cm⁻¹, there is good evidence for \( \eta^2 \).
CCH(a) (see Chart 4). In the chemistry of C₂H₃I on Pt(111), ethylidyne [CCH(a)] forms below and partially dehydrogenates above 450 K, producing two H₂ desorption peaks (520 and 650 K).⁶ As here, the partially dehydrogenated species gives losses at 835 and 3035 cm⁻¹. Ethylene on Pt(111), heated to 620 K, dehydrogenates to leave a stoichiometry of C:H = 2:1 and two losses at 850 and 3100 cm⁻¹.⁷ The nature of the intermediate(s) has been, however, somewhat controversial. Baro and Ibach⁷⁵ proposed C(a) and CH(a). Salmeron et al.⁹⁰ and Davis et al.⁷⁰ proposed mixtures of CCH(a), CH(a), and C(a) from their TPD and ¹⁴C crossreactor study. Zhou et al.⁷¹ using SSIMS, provided evidence for C–C bonds throughout the entire dehydrogenation process. Recent work by Land et al.⁷² using STM, showed C–C bonds (clusters) upon completion of ethylidyne dehydrogenation (700 K) and graphite island formation at higher temperatures. Thus, while some CH(a) may be present, the evidence favors CCH(a) as the dominant species between 540 and 640 K. The fact that both the decomposition of CCH(a) and the reaction of CICHJ on Pt(111) give the same HREELS spectra above 500 K indicates that, in the latter case, CCH(a) is also a likely intermediate.

A simple comparison of the electron energy losses at 830 and 3035 cm⁻¹ (Figure 8) with literature⁷⁷⁻⁷⁸ (see Table 4) may lead, erroneously, to the conclusion that the new surface species above 450 K is also CH(a). To support this conclusion, one would have to argue that a rehybridization from sp³ to sp² of the carbon in CH(a) had occurred. However, such a rehybridization is not thermodynamically favored.⁷³

On the other hand, introducing η²-CCH(a) makes for a consistent picture. Forming CCH(a) is thermodynamically favored (ΔH = -20 kcal/mol).⁷⁴ The carbon atoms in η²-CCH-

(73) For sp³ CH on Pt(111), there are three σ Pt–C bonds worth 159 kcal/mol, and for sp² CH there are two σ Pt–C bonds worth 106 kcal/mol.⁷⁴ If the C–H bond is perpendicular to the surface, the p orbital of the sp² carbon is parallel to the surface, and its interaction with Pt 6s and 5d orbitals will be negligible. The orbital interaction can be increased by tilting the C–H bond from its perpendicular position (Chart 3) but will not reach that between the sp³ orbital of carbon and Pt 6s and 5d orbitals. By analogy, σ(C–C) bonds are always weaker than σ(C–C) bonds.
saturation CH₂(a) coverage produced from CH₂N₂ is at least four times higher than produced by dissociation of CICH₂I. However, CH₄ was still observed in TPD when only 0.048 ML CH₂I was adsorbed on Pt(111). Local coverage remains an attractive possibility; for CICH₂I decomposition, the CH₂ fragments may seldom escape from halogens which, through steric effects, could inhibit recombining formation of CH₂H₄. While the role of halogens may be important here, it is not universal. On Ag(111), Cu(110), and Pd(100), 4 coupling of CH₂(a) to form CH₂H₄(g) occurs readily in the presence of coadsorbed halogens.

Dihydrogen formation and desorption is not altered significantly by the presence of halogens; both diazomethane and chloroiodomethane lead to two identical H₂ peaks above 500 K and to distinguishable H₂ desorption only at lower temperatures (200–290 K). In our case, the low temperature H₂ peak (220 K) is reaction-limited (i.e., kinetically controlled by the dehydrogenation of CH₂(a) and/or CH₂Cl(a)). It is weak because much of the H(a) is removed at lower temperatures as either HCl or CH₂Cl. For CH₂H₄, the low temperature H₂ peak (290 K) was attributed primarily to dehydrogenation and subsequent rearrangement of CH₂H₄ to C₂H₂. We find that CH₂ starts to dehydrogenate at 180 K but becomes rapid only above 200 K. Assuming the same for CH₃ derived from CH₂N₂, then part of the 290 K H₂ desorption is attributable to C–H cleavage at lower temperature, i.e., it is not solely due to dehydrogenation of CH₂H₄ to form C₂H₂. This is supported by the fact that, when H₂ was coadsorbed with CH₂N₂ on Pt(111), the dosed hydrogen also desorbed at 290 K.

At higher temperatures, we have presented evidence that the 640 K peak is attributable to CCH(a) decomposition; the same species likely controls the high temperature region when diazomethane is used. The 520 K peak is attributed to different dominant sources in the two cases—CH₂(a) in the case of CH₂N₂ and CH₂(a) for chloroiodomethane. As mentioned earlier, the dehydrogenation of C₂H₄ on Pt(111) produces two H₂ peaks just as CH₂(a) does. Obviously, similar TPD spectra, by themselves, do not establish that the same intermediates are in control. However, our TPD and HREELS data indicate that complete decomposition of CH₂(a) to C(a) does not occur below room temperature and, since there is no evidence for C₂H₄ accumulation, we have proposed CH₂(a). While halogens may inhibit ethylene and ethylidyne formation in our case, we see no reason to suppose that CH₂(a) formation should not participate in the decomposition of CH₂ derived from CH₂N₂. Clearly, direct measurement of intermediates formed from CH₂N₂, e.g., using HREELS, would be very worthwhile.

Like dihydrogen, methane desorption is similar for both adsorbates; strong peaks with shoulders are evident in the 200–270 K regime (Although not discussed, a close look at the TPD spectrum after CH₂N₂ exposure, suggests a shoulder at about 200 K; it is clearer when H is coadsorbed.) This result indicates that the presence of halogens does not dramatically alter the pathway leading to methane. We take this as consistent with the notion that neither C–H bond breaking nor diffusion to hydrogenate CH₄ are inhibited by halogens.

It is interesting that another adsorbate, CH₃I, gives H₂ TPD very much like those for CH₂N₂ and CICH₂I—three H₂ desorption peaks (320, 520, and 640 K). There is general agreement that the 320 K H₂ peak is limited by recombination of H(a) formed from the dehydrogenation of CH₃I at lower temperatures. Earlier work attributed the two higher temperature peaks to dehydrogenation of CH₂(a) or CH(a), but we have proposed dehydrogenation of CH(a) and CCH(a) fragments, respectively, because our data indicate that CH₂(a) is not stable over 300 K. There is positive infrared identification of CH₂ only up to 280 K. Since dehydrogenation and subsequent hydrogenation of CH₂(a) to form methane occur in this same temperature regime, methane formation from CH₃I is sensible and consistent with our proposal (see scheme 1). We believe that, whether CH₃ or CH₂ is the initial species on Pt(111) at low temperatures, the final thermal reaction intermediates are the same—CH(a) and CCH(a).

Continuing to compare iodomethane and chloroiodomethane, there are some differences in H₂ desorption at low temperatures. At saturation, CICH₂I gives a very small H₂ peak at 220 K, while CH₃I gives a larger H₂ peak at 320 K. Local coverage appears to be important—as C–I and C–Cl bonds break in the presence of a locally crowded surface, atomic hydrogen is displaced and recombined immediately to desorb dihydrogen.

For CICH₂I, the available H(a) is consumed to form CH₂Cl, also at 220 K, making the H₂ desorption in this region negligible.

4.2. Reactions of CICH₂I with D(a). Within the above framework, the impact of coadsorbed D is readily understood. At low temperatures, D enhances the competitiveness of parent desorption with respect to dissociation. In fact, according to Figure 11, coadsorbed D lowers the thermal activation needed for parent desorption. Since dissociation starts at about 150 K, with or without D(a), the fraction of parent desorbing increases. Even when dissociation occurs, coadsorbed D(a) diminishes the extent to which C-containing fragments end up as fully dehydrogenated surface carbon. Competitive and reversible dehydrogenation and hydrogenation of CH₂(a) and CCH(a) accounts for this, i.e., increasing the chemical potential of atomic hydrogen increases hydrogenation.

It is interesting that, besides the dominant deuteration products (CH₂D and CH₂DCI), there are also H-D exchange products for methane (CHD₃ and CD₄) but not for methyl chloride. Model structures accounting for this distinction are presented in scheme 2 (The scheme does not imply that adsorbed D promotes C–H and C–Cl bond dissociation.). For CH₃C(a), we suppose that the carbon–surface bond is tilted, allowing the Cl atom to interact with the surface, and keep the H atoms away from it. From this geometry, the transition state involving D leads to either CH₂DCl, which desorbs, or CH₃D(a) and Cl(a). Once broken, the C–Cl bond does not reform. Through the entire reaction process that forms methyl chloride, the two original C–H bonds remain, i.e., neither CHD₂Cl nor

| Table 5. Vibrational Frequencies (cm⁻¹) Assigned to CCH Species |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| mode | C₁H/C₂H₂I/Pd(111) | C₁H/C₂H₂I/Ru(001) | C₁H/C₂H₂I/Pd(111) | C₁H/C₂H₂I/Ru(001) |
| ν(CH) | 3035 | 3035 | 2960 | 2995 |
| ν(CC) | 1300 | 1290 | 1360 | 1360 |
| δ(CH) | 830 | 835 | 750 | 750 |
| ν(CH) | 465 | 490 | 430 | 430 |
| ν(CH) | 380 | 370 | 370 | 370 |

\(^{a}\) This work. \(^{b}\) Reference 6. \(^{c}\) Reference 58. \(^{d}\) Reference 76 and 77. \(^{e}\) Reference 77. \(^{f}\) Reference 78. \(^{g}\) Reference 79. \(^{h}\) Reference 80. \(^{i}\) Reference 81. \(^{j}\) Doubles. \(^{k}\) A broad peak between 1100 and 1500 cm⁻¹.
CD$_3$Cl form. On the other hand, when CH$_2$ incorporates D(a), the transition state leads to either CH$_2$D(a) (hydrosygenation) or CHD(a) (exchange). Repeated arrival at this transition state would lead to both CHD$_3$ and CD$_4$, the distribution being independent evidence for D-for-H exchange in CH$_3$ groups; there is no concentration of D in the methane drops. The 355 K methane peak is also similar. Not surprisingly, the D concentration is highest in the lowest temperature peak (194-198 K, Figures 12 and 13). Toward higher temperatures, D(a) is consumed, H(a) is supplied, and the concentration of D in the methane drops. The 355 K methane peak is interesting. Up to a limit, the total desorption in this region intensifies as the initial D(a) coverage increases (compare Figures 3 and 12), but this peak disappears when D(a) is high (Figure 13). For an initial coverage of 0.15 ML D(a), we estimate, from the methane (CH$_4$, CH$_3$D and CD$_2$H$_2$) peak at 355 K and the HCl peak at 360 K, that a total of 0.01 ML (CH$_3$H, CHD(a), and CD$_2$(a)) remains above 300 K, compared to 0.02 ML on the D-free surface. Nevertheless, because less Cl(a) is present at 355 K to abstract H from CH$_2$(a) to form HCl, more methane is produced, even though the total methylene coverage is lower. Overall, the methane formation here is very similar to that observed when CH$_3$N$_2$ was coadsorbed with H(a).

The isotopic content of the 355 K methane peak is also interesting. Figure 12 shows that, even though the H(a) and D(a) present at low temperatures recombine and desorb near 230 K, there is significant D(a) content in the 355 K methane peak. We take this as indicating the formation of a significant concentration of CD$_x$ (x = 1, 2) below 240 K, presumably through an exchange like that illustrated in Scheme 2.

### 4.3. Reactions of ClCH$_2$I with Atomic O.

As atomic oxygen is added, perturbation of the parent ClCH$_2$I desorption becomes apparent but only for O(a) ≥ 0.035 ML; the multilayer peak, as expected, remains fixed at ca. 160 K, but the monolayer peak broadens toward higher temperature and splits into at least two identifiable local maxima (240 and 305 K). Because XPS confirms the presence of both C=I and C−Cl bonds, even at 290 K, and because HREELS indicates some molecular ClCH$_2$I at 285 K, the ClCH$_2$I TPD peak at 305 K is attributed to molecular ClCH$_2$I species rather than the recombination of dissociated ClCH$_2$I. Stabilization by O(a) can be readily understood as a donor−acceptor interaction. Like other alkyl halides, ClCH$_2$I lowers the surface weak function, i.e., is an electron donor. Atomic oxygen, on the other hand, is an electron acceptor and increases the surface work function of Pt(111). Compared to clean Pt(111), some sites become electron deficient in the presence of O(a), and, as a result, the interaction with ClCH$_2$I increases. The destabilization effect of coadsorbed D can be understood in the same way; atomic D is an electron acceptor and increases the surface work function of O(a). More interesting is the participation of O(a) in the reaction chemistry of ClCH$_2$I, particularly the formation of oxidation products. For very low initial O(a) coverages, water (220 K) and carbon monoxide (450 K) desorb, but carbon dioxide and formaldehyde are absent. These products, and CH$_2$Cl$_2$, begin to appear for O(a) ≥ 0.035 ML (recall that saturation O(a) is 0.25 ML). XPS indicates that, just as in the absence of O(a), dissociation starts with C−I bond cleavage below 170 K. The low onset temperature (~155 K) for CH$_2$O desorption indicates that a few C−Cl bonds are activated below 170 K.

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However, C–Cl cleavage is not evident in XPS and HREELS, so we conclude that C–Cl bond breaking, accompanied by partial oxidation to formaldehyde, occurs to a much less extent than C–I bond breaking. We suggest that desorption, rather than oxidation, of CH₂O is the result of a stoichiometric shortage of O(a) and a locally high coverage of halogens (Cl and I) which weakens the bonding of CH₂O(a) to the surface. Above 0.35 ML O(a), this trend continues, but complete oxidation to CO₂ becomes more important. Further, no C–H bonds are retained beyond 500 K for oxygen coverages higher than 0.19 ML. HREELS indicates accumulation of CICH₃, and, in TPD, CH₂Cl increases sharply.

While increasing O(a) reduces the intensity of the CH₃Cl, CH₄, and HCl TPD peaks, the peak temperatures are constant (Figure 17). These features can be described in terms of reactions and sites that are not perturbed by O(a). Obviously, other sites and reactions are dependent on O(a), e.g., O(a) competes for available H(a) and stabilizes some CICH₃I and CICH₂Cl₂, preserving C–Cl bonds to temperatures where reactions leading to chlorination to Cl₂H₂ and partial oxidation to CH₂O can compete with HCl, CH₄, and Cl₂Cl formation. Starting with saturation O(a) (0.25 ML), the broad I(3d₅/₂) XPS peak, observed at 250 K, corresponds to 45% I(a) and 55% molecular CICH₃I(a), compared to 100% I(a) when O(a) is absent. Since no O-containing reaction intermediates associated with the oxidation products were identified with HREELS, we conclude that evolution of these products is reaction-limited and involves CH₂(a) or CH₂Cl(a) since both are present in spectroscopically significant concentrations between 210 and 285 K. Methoxy, CH₂O(a), can be ruled out because no methanol is found in TPD. From all the XPS and HREELS evidence, it appears that dissociation of C–I and C–Cl and the formation of CH₂O can proceed simultaneously, resulting in only small changes in the CH₃(a) and CH₂Cl(a) concentrations between 210 and 285 K.

The TPD for CH₂O, H₂O, HCl, CO₂, CH₂Cl₂, and CICH₃ all peak at the same temperature, 305 K, and, for CH₂O, HCl, CH₂Cl₂, and CICH₃I, cut off sharply at 320 K. In traversing the temperature range between 170 and 320 K, XPS and HREELS data indicate the following: (1) CICH₃I dissociates, (2) the CH₂(a) (770 and 2940 cm⁻¹) concentration increases, (3) the Cl(a) concentration remains nearly the same, and (4) at 320 K, the surface coverage includes a small quantity of CH₂(a) but no CICH₃I(a). Based on this information, we propose the following, not necessarily elementary, reactions to form these products:

\begin{align*}
H(a) + Cl(a) & \rightarrow HCl(g) \\
CH₂Cl(a) + Cl(a) & \rightarrow CH₂Cl₂(g) \\
2H(a) + O(a) & \rightarrow H₂O(g) \\
CH₂(a) + O(a) & \rightarrow CH₂O(a) \\
CH₂O(a) & \rightarrow CH₂O(g) \\
CH₂O(a) & \rightarrow CO(a) + 2 H(a) \\
CH₂O(a) + O(a) & \rightarrow OCHO(a) + H(a) \\
-0CHO(a) & \rightarrow CO₂(g) + H(a) \\
CO(a) + O(a) & \rightarrow CO₂(g)
\end{align*}

Alongside these reactions, there is decomposition eventually leading to CCH₂(a) (Figure 20) and C₆(a), as in Scheme 1. We propose that CH₂O(a), in di-σ-bonded form, -CH₂O-, is the key intermediate that leads to formaldehyde, carbon monoxide, and carbon dioxide. The distribution of these products is determined by the local oxygen and halogen coverages; when oxygen is in short supply, partial oxidation of CH₂(a) followed by desorption (reactions 4 and 5) dominate. When the local concentration of oxygen is high, formate (OCHO, reaction 7) forms and promptly decomposes, leading to the sharp 305 K peak for CO₂. While the cut-off (320 K) is the same for CH₂O, H₂O, and CO₂, CH₂O sets in at lower temperatures than either water or carbon dioxide. This can be understood in terms of two kinetically competitive reaction channels for the -O–CH₂-. Below 280 K, rearrangement and desorption as CH₂O dominates, i.e., lower activation energy. Above 280 K, reaction to form CO(a) or OCHO(a) begins to dominate. CO₂ is released either from the dehydrogenation of OCHO(a) or the oxidation of CO. Water is produced from the released H(a). This proposal is consistent with the literature. Formate decomposes between 210 and 280 K, producing CO₂(g) and H(a). Methoxy (CH₂O(a), in the presence of O(a), undergoes dehydrogenation to CO and H beginning at 170 K, and CO₂ evolves at 320 K. CO oxidation sets in around 260 K. Interestingly, whereas CH₂O normally absorbs dissociatively to form CO and H at 105 K, in our case, coadsorbed halogens modify the surface, so that the decomposition channel of -OCHO- does not become competitive with desorption until about 280 K. Because both the decomposition of -OCHO- and the oxidation of CO occur at lower temperatures than the proposed reactions that form -O–CH₂- (a), spectroscopically significant concentrations of CO(a) and -OCHO-(a) do not accumulate, e.g., in Figure 20, there is no evidence for any CO(a).

The peak for parent CICH₃I at 305 K and, particularly, the sharp cut-off at 320 K suggest that dissociation of CICH₃I induces the desorption of neighboring species in a process similar to that proposed for the thermal and photodesorption of O₂ from Ag(110). As shown in Figure 20, heating the surface from 320 to 370 K eliminates all CH₃(a), decreases the amounts of CH₂(a), Cl(a), and O(a), and causes the formation of CCH₂(a) (850 and 3050 cm⁻¹). The species desorbing in this temperature regime are HCl, H₂O, and CO₂. In this temperature interval, CO₂ formation is best described in terms of CH(a) oxidation, accompanied by water formation, i.e., there is HREELS evidence for O(a) and CH(a) but not CO(a). HCl is formed by abstraction of H from CH₂(a) or CH₃(a). Methylene may also react with oxygen to form CH(a) and OH(a), the latter promptly forming water. As shown in Figure 17 (panels E, F, and I), when O(a) increases, the intensities of the 360 K peaks for H₂O and CO₂ increase, but the H₂ peak due to CH₂(a) dehydrogenation decreases and disappears for O(a) ≥ 0.12 ML. We conclude that for a saturation does of CICH₃I coadsorbed with O(a) ≥ 0.12 ML, CCH₂(a), but not CH₂(a), exists above 400 K. In the absence of O(a), CCH₂(a) does not form at 370 K. Thus, O(a) lowers the activation barrier for CCH₂(a) formation, probably by scavenging H atoms and, in so doing, promotes the reaction to form the thermodynamically favored CCH₂(a).
the formaldehyde evolution trails H$_2$O by about 15 K ($\sim$3 s). Assuming C--H bond cleavage determines the rate of H$_2$O evolution, i.e., H(a) diffuses rapidly, then a delay in the evolution of CO is understandable on the basis that it is relatively difficult to oxidize the resulting C$_2$ or larger C clusters, i.e., oxidative cleaning of carbon on Pt requires temperatures exceeding 1000 K.

Above 400 K, the following multistep reactions are, thus, inferred:

\[
\begin{align*}
2\text{CCH}(a) + \text{O}(a) & \rightarrow \text{H}_2\text{O}(g) + 2\text{C}_2(a) \text{ at 410 K} \\
\text{C}_2(a) + 4\text{O}(a) & \rightarrow 2\text{CO}_2(g) \text{ at 425 K} \\
\text{C}_2(a) + 20\text{O}(a) & \rightarrow 2\text{CO}(a) \text{ around 425 K} \\
\text{CO}(a) & \rightarrow \text{CO}(g) \text{ 445 K} \\
\text{xCCH}(a) + \text{xCl}(a) & \rightarrow \text{xHCl}(g) + \text{C}_2(a) \text{ at 460 K}
\end{align*}
\]

Because the initial oxygen is all consumed and desorbed at lower temperatures, the last of these reactions removes the final amounts of H. In the absence of initial O(a), the last H is removed as H$_2$ (Figure 5). The small CO peak at 445 K, even though not detected by HREELS, is probably desorption limited because CO adsorbed on 1-covered Pt(111) desorbs at this temperature.$^6$ In the same regime, 415--440 K, desorption-limited CO was observed from oxidation of C$_2$H$_2$.$^{91}$ C$_2$H$_4$ and CH$_2$N$_2$.$^{28}$ on Pt(111).

We now compare the oxidation of CICH$_2$I and CH$_2$N$_2$. For a saturation dose of CH$_2$N$_2$ on 0.21 ML O(a), TPD showed three peaks, 185, 235, and 330 K, for H$_2$O, a peak at 330 K from dehydrogenation of CH$_2$(a). Second, the broad H$_2$O and CO$_2$ peak at 330 K from CH$_2$N$_2$ (which split under certain conditions) correlates with the H$_2$O and CO$_2$ peaks at 305 and 360 K from CICH$_2$I. The 330 K peak for H$_2$O and CO$_2$ from CH$_2$N$_2$ could result from the oxidation of CH$_2$(a) and/or CH$_3$(a) via an $-\text{OH}$$^-$--CH$_2$(a) intermediate like the one we have proposed (note that the evolution of CH$_2$ at 330 K indicates the existence of CH$_2$(a)$^{28}$). We suggest that, in the absence of adsorbed halogens, the dehydrogenation and further oxidation of $-\text{OH}$$^-$--CH$_2$(a) overwhelms CH$_2$(a) desorption. Because the CH$_2$(a)/O(a) ratio for the CH$_2$N$_2$ case is relatively high, there is no O(a) left at high temperature with which to oxidize CICH$_2$I. Thus, no CO$_2$ and H$_2$O evolves above 400 K. There is a third similarity: a small CO peak desorbs around 450 K.

Before closing this section, we comment briefly on the oxidation of CICH$_2$I from the environmental point of view. Ideally, the oxidative destruction of halogenated hydrocarbons should lead exclusively to CO$_2$, H$_2$O, and HX. The formation of CH$_2$Cl$_2$ indicates that on Pt(111) C--Cl bond formation can compete with C--O bond formation and lead to small amounts of undesirable products unless a huge excess of oxygen is used.

**4.4. Effect of Halogens on CH$_2$ Reactions.** It is well-known that halogens influence catalyst selectivity. For example, traces of chlorinated hydrocarbons are typically added to the reactant feed of oxygen and ethylene in order to improve the selectivity of Ag/Ag$_2$O catalysts for ethylene oxide.$^{52}$ Again, while unpromoted Pd is a catalyst for the complete combustion of methane to CO$_2$ and H$_2$O,$^{10}$ selectivity for partial oxidation of methane to CO$_2$ and H$_2$O occurs in the presence of halogenated hydrocarbons.$^{97,98}$ As here, adsorbed halogen atoms, produced by dissociation, are key$^{97,98}$ and exert their influence through both geometric and electronic effects. For example, the Cl atoms on Ag(110) block the dissociative adsorption of O$_2$ (geometric effect) and enhance the adsorption of C$_2$H$_4$ by creating Ag$_{44}$ sites (electronic effect).$^{95}$ Following these results, we suppose that the absence of CH$_2$O formation in the diazomethane--oxygen--Pt(111) system,$^{28}$ and its presence in our work for chloroiodomethane--oxygen--Pt(111) indicates a key promotion role for the halogens. The promotion mechanism for CH$_2$O formation by Cl(a) and I(a) remains to be established, and our observations may motivate studies of how preadsorbed halogens alter the surface electronic structure of Pt(111) and how they influence the adsorption (including coadsorption with oxygen) and reaction of relevant species, e.g., CH$_2$O, CH$_3$OH, CO, H$_2$, and CH$_2$.

While Cl(a) and I(a) have a significant promotion effect on CH$_4$O formation, they have little influence on the dehydrogenation and hydrogenation of CH$_2$(a) because, as noted above, CH$_4$ formation and desorption is comparable for CH$_2$N$_2$ and CICH$_2$I. To account for our observations, we propose Chart 5 (where Cl(a) and I(a) are assumed to possess negative charge in some cases) and the desorption of CH$_2$(a) from environmental point of view. However, it is reasonable and useful for illustrative purposes. With this framework, its desorption must be competitive with dehydrogenation of $-\text{OH}^-$--CH$_2$(a) if CH$_2$(a) is to appear. Since dehydrogenation of CH$_2$O on clean Pt(111) occurs at 105 K,$^{156}$ our data suggests that adsorbed halogens suppress the activity of this process. We assume little or no

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diffusion for \([-\text{OCH}_2-]\) below 280 K. For a structure like Chart 5A, those Pt atoms adjacent to the C–H bonds are occupied by Cl(a) and I(a) and, thus, are strongly modified, i.e., we assume short-range effects dominate. In this case, the C–H bond cleavage is inhibited because either the nearest Pt atoms are passivated so that the effective activation energy for cleavage of the C–H bonds in \([-\text{OCH}_2-]\) is high or they are thermodynamically less favorable (on energetic and/or steric grounds) sites for occupation by H atoms. Therefore, desorption of CH₂O becomes kinetically competitive with dehydrogenation. Alternatively, in Chart 5B, Cl(a) and I(a) are placed next to the O atom in \([-\text{OCH}_2-]\) and the Pt atoms adjacent to the C–H bonds are not strongly modified. In this case, the C–H bonds break readily making desorption of CH₂O less competitive. Above 280 K, the diffusion of \([-\text{OCH}_2-]\) may become significant; if so, the geometry of Chart 5A can be easily converted to that of Chart 5B and lead to the thermodynamically favored products, CO₂ and H₂O, at the expense of CH₂O.

Two intuitively plausible bonding geometries for CH₂(a) are shown in Chart 5 (parts C and D). Here, we assume that Cl(a) and I(a), formed from ClCH₂I dissociation, are not far apart (which is very likely the case because desorption of atomic I and Cl from Pt(111) does not occur until about 800 K so diffusion around 200 K would be slow). In both parts, CH₂(a) can dissociate easily to form CH(a) and H(a), provided the electronic effects of Cl(a) or I(a) are not strongly inhibitory. In the absence of coadsorbed halogens, e.g., CH₂N₂, C₂H₄ forms indicating that CH₂(a) is activated and can recombine, even below 200 K. Thus, short range mobility/reorientation between the geometry of 2C and 2D is plausible. The pairing of CH₂(a) requires, however, longer-range diffusion which, in the presence of Cl(a) and I(a), may be sterically inhibited, accounting for the absence of ethylene in our case.

5. Conclusions

At or below 100 K, ClCH₂I adsorbs molecularly on Pt(111). In subsequent TPD, the physisorbed layers desorb intact at 160 K. In the first monolayer, however, both parent desorption and irreversible dissociation takes place. The fraction depends strongly on the initial coverage; dissociation is exclusive for low doses. For doses that exceed 50% of the first layer, there is parent desorption with peaks at 175 and 233 K. Dissociation begins by breaking the C–I bond (onset at ~150 K), followed by the C–Cl bond (onset at ~170 K), and C–H bonds (onset at ~180 K). The resulting intermediate products include adsorbed I, Cl, CH₂Cl, CH₂, and CH. Complete decomposition of ClCH₂I to form H₂(g), HCl(g), I(a), and C₂(a) dominates for low ClCH₂I coverages. At high coverages, reactions forming
CH₄ and CH₂Cl become important. The estimated first layer coverage is 0.18 ML (molecules of ClCH₂I per Pt). Of this, 28% (0.05 ML) desorbs molecularly, and 72% (0.13 ML) undergoes dissociation and yields 0.109 ML HCl, 0.007 ML CH₄, 0.019 ML CH₃Cl, 0.065 ML of atomic H (desorbing as H₂ after background subtraction of 0.03 ML), and 0.102 ML carbon. The hydrogenation of CH₂Clₐ to form CH₃Cl by background H(a) starts at 150 K and peaks at 190 K, while that by H atoms supplied from CH₂(a) dehydrogenation starts at about 180 K and peaks at 210 K. The hydrogenation to CH₃Cl and the dissociation to Cl(a) and CH₂(a) of CH₂Cl(a) are kinetically competitive. The hydrogenation of CH₂(a) to form CH₄ by background H(a) starts at 170 K, while the self-hydrogenation of CH₂(a) to CH₄ starts at about 180 K and peaks at 220 K. HCl and H₂ formation and desorption are rapid at 220 K. While the dissociation of C—I and C—Cl bonds is complete and most of the resulting CH₂(a) fragments react below 260 K, a small fraction of CH₂(a) is stable up to 360 K where it undergoes both self-hydrogenation and reaction with Cl(a) to form gaseous CH₄ and HCl and surface CH. The reaction of Cl(a) with CH₂(a) to form HCl(g) and CCH(a) occurs at 415 K. All the remaining CH(a) reacts at 520 K to release H₂(g) and form C(a) and CCH(a). The decomposition of CCH(a) to form H₂ and more C(a) occurs between 600 and 700 K. Surface iodine desorbs atomically between 800 and 900 K. A comparison of our HREELS data with those obtained from C₂H₄ and C₂H₃I, where ethylidyne is involved, suggests that CCH(a) is formed when ethylidyne begins to decompose.

The influence of coadsorbed D atoms is noted in several ways; D(a) (1) lowers the heat of adsorption of ClCH₂I; (2) suppresses parent dissociation slightly; (3) suppresses, for those ClCH₂I admolecules undergoing dissociation, complete decomposition leading to C(a); and (4) promotes the reaction channels to methane and methyl chloride. The reaction between dissociated ClCH₂I and D produces not only deuterated methane (CH₃D and CH₂D₂) and methyl chloride (CH₃Cl) but also H–D exchanged methane (CHD₃ and CD₄). Interestingly, no H–D exchanged methyl chloride (i.e., CHD₂Cl and CD₂Cl) was found. The D/H ratio in methane and methyl chloride increases with the preadsorbed D coverage.

Coadsorbed O atoms influence the adsorption and reaction of ClCH₂I in the following ways: (1) increase the heat of adsorption of ClCH₂I; (2) suppress parent dissociation slightly; and (3) decrease the yield of the CH-containing reaction products. With 0.25 ML O(a), two kinds of chemisorbed ClCH₂I are evidenced—bound to Pt that is or is not perturbed by O(a). The unperturbed sites lead to CH₄, CH₂Cl, HCl, and H₂O desorption below 250 K. The perturbed sites lead to desorption of oxygenated and chlorinated products above 250 K, e.g., H₂O, CO₂, CO, CH₂O, HCl, and CH₂Cl₂. CH₂O forms below 320 K through the reaction of O(a) with CH₂ and/or CH₂Cl fragments; the proposed intermediate is –O–CH₂–(a). CH₂Cl₂ results from the chlorination, between 250 and 320 K, of CH₂Cl fragments. The oxidation of CH₂ and/or CH₂Cl to form H₂O and CO₂ occurs at 305 K; –O–CH₂— and –O–CH–O— are proposed as key intermediates. The oxidation of CH₂Cl(a) to H₂O and CO₂, and of CCH(a) to CO, occurs between 320 and 400 K and between 400 and 450 K, respectively. When the coverage of coadsorbed O(a) is higher than 0.19 ML, some Cl(a) remains on the surface up to 800 K where it desorbs atomically. That CH₂O desorbs in this study, but not when diazomethane is used, points out the importance of halogens as catalytic promoters that improve the partial oxidation selectivity of transition metals.

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