Preparation and Reactivity of Alkyl Groups Adsorbed on Metal Surfaces

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Heterogeneously catalyzed reactions constitute the basis of most chemical and fuel technologies. The conversion of hydrocarbons in particular is at the heart of the refining of crude oil, the modification of fat in food industries, and the synthesis of pharmaceutical products and fine chemicals. Unfortunately, since catalytic processes are generally quite complex, little is known about the individual steps that take place at the molecular level in such systems. It is only recently that the advent of a variety of modern surface-sensitive instrumentation has made those studies feasible;[1] the power of using such techniques in elucidating reaction mechanisms has been shown already in several key cases.[2,3]

In spite of the recent technological advances mentioned above, the details of the processes involved in the conversion of saturated hydrocarbons are still not well understood. The activation of those compounds is believed to occur through an initial C–H bond scission step that results in the formation of alkyl groups on the surface. However, since that reaction often displays quite low probabilities, catalytic processes need to be performed under fairly severe pressure and temperature conditions in order to reach reasonable conversion rates. High pressures are not easy to reproduce in the vacuum environments normally used in surface science studies, and in addition, they tend to accelerate the conversion of alkyl groups into other species, making the steady-state concentration of those intermediates on the catalyst surface too low to be detected.

Several approaches have been taken in order to overcome the difficulties mentioned above. One way to make C–H bond breaking reactions easier under vacuum is by using open surfaces with low-coordination metal atoms, because those sites tend to display higher reactivity.[4] Alternatively, supersonic beams can be used to deliver gas molecules having the high energies needed for their activation.[5,6] However, even though studies based on these ideas have yielded very exciting results, they have proven less than general for investigating the surface chemistry of hydrocarbons on surfaces.

Recent studies in my laboratory and a few others have shown the feasibility of yet another method for preparing chemisorbed alkyl groups, namely, by dissociating alkyl halides adsorbed on surfaces. It is well-known that alkyl radicals can be efficiently prepared in either gas or liquid phases by activating suitable precursors such as alkyl halides, azo compounds, and peroxides.[7] Alkyl halides are particularly good candidates for studies on surfaces because they are easy to prepare and to handle under vacuum and because they have already been shown to undergo oxidative addition reactions in solution to form organometallic products with alkyl ligands attached directly to the metal center.[8] Over the past few years we have characterized the chemisorption and reactivity of alkyl halides on transition metals using a combination of modern surface-sensitive techniques on well-defined single crystals. In this account we summarize what we have learned so far from those studies.

Table I
Literature Survey of the Surface Characterization Studies Done on the Chemisorption and Surface Activation of Alkyl Halides

surface	molecule	activation	ref
W(100)	CH_3Cl, CH_3Br, CH_3I	thermal	9
Fe(100)	CH_3Cl	thermal	10
Ru(100)	CH_3I	thermal	11
polycrystalline Co	CH_3Cl, CH_2Cl_2	thermal	12
Ni(100)	CH_3Cl, CH_3Br, CH_3I, C_2H_5I, C_3H_7I	thermal	13–15
Ni(111)	CH_3Br	photolytic	16
Pd(100)	CH_3Cl	thermal	17, 18
	CH_3Cl	photolytic	19
Pd(111)	$ClCH_2CH_2Cl$	photolytic	20
Pt(111)	CH_3Cl, CH_3Br, CH_3I, C_2H_3Br, C_2H_3I, C_2H_5Br, C_2H_5I	thermal	21–26
	CH_3Cl, CH_3Br, CH_3I, C_2H_5I	photolytic	27–30
Cu(110)	CH_3Cl, CH_3I, CH_2I_2, C_3H_7I	thermal	31, 32
Ag(111)	CH_3Cl, CH_3Br, CH_3I, CH_2ICl, C_2H_3I, C_2H_5I, C_3H_7I, $Cl(CH_2)_3I$	thermal	33–35
	CH_3Br, CH_3I, C_2H_5Cl	photolytic	36–38
Ag(110)	CH_2I_2	photolytic	39
polycrystalline Au	CH_3Cl	thermal	40
Al(111), Al(100)	C_2H_5I, C_3H_7I, C_4H_9I, $C_6H_{13}I$	thermal	41

Experimental Considerations

Surface reactions are now routinely studied under ultrahigh-vacuum conditions (UHV, 10^{-10}–10^{-11} Torr) in order both to facilitate the use of electron- and ion-based spectroscopies and to keep the sample clean from contaminants. Many surface-sensitive techniques have been developed in the past few decades for this purpose; the ones most commonly used in our experiments include thermal programmed desorption (TPD), X-ray

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photoelectron spectroscopy (XPS), static secondary ion mass spectrometry (SSIMS), electron energy loss spectroscopy (HREELS), and reflection–absorption infrared spectroscopy (RAIRS). Single crystals are often chosen as substrates because their surfaces can be characterized in more detail than those of polycrystalline samples. The crystals are initially cleaned under vacuum either by chemical treatment or by ion bombardment–annealing cycles until no impurities are detected on the surface; this allows for the performance of experiments starting with very well defined systems. A detailed description of the techniques and procedures involved in this type of studies can be found readily in the existing literature.[1]

Chemisorption of Alkyl Halides

The chemisorption of alkyl halides has already been studied on a wide variety of surfaces (Table I). The experimental data available so far indicates that adsorption at low temperatures is molecular. Three main pieces of evidence support that conclusion: First, desorption of intact molecules can be thermally driven from most surfaces even at coverages below saturation; second, ion bombardment of those surfaces at low temperatures yields secondary ions with molecular stoichiometry; and finally, the vibrational spectra of the chemisorbed species are quite similar to those of the original molecules.

The adsorption geometry of adsorbed alkyl halides has also been studied in some detail. XPS experiments indicate that bonding to the surface occurs through the halogen end of the molecule: the binding energies of electrons associated with the halide atom shift by up to 1 eV upon chemisorption while the values for the C 1s electrons remain unaffected.[15,22,24] In addition, the molecular axes of the hydrocarbon fragments change orientation in going from below to above half saturation coverages.[23] An example of this behavior is illustrated by the RAIRS spectra of ethyl bromide adsorbed on Pt(111) shown in Figure 1: while at low coverages, the methyl groups are oriented parallel to the surface; they rearrange to a perpendicular configuration upon further exposure. Similar results have been obtained for other systems.[23,24,42,43]

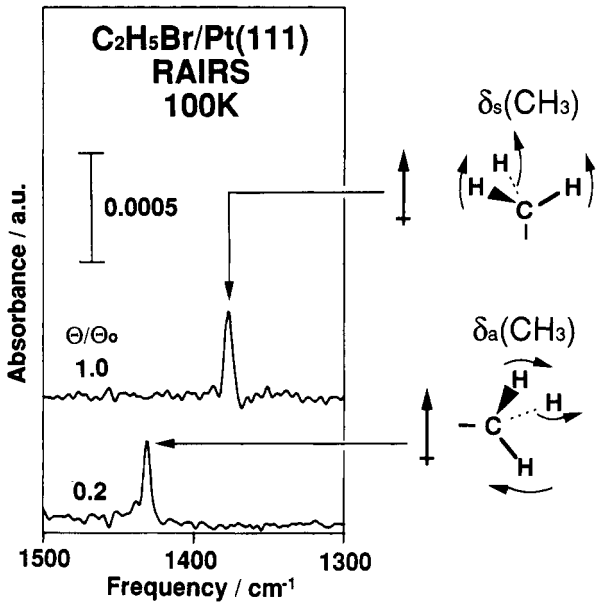

Figure 1. Reflection–absorption infrared (RAIRS) spectra for ethyl bromide adsorbed on a Pt(111) surface at 100 K. The two traces shown, which correspond to coverages of 20 and 100% of saturation, illustrate how the surface selection rule obeyed by RAIRS can be used to determine adsorption geometries. Only one peak due to the asymmetric deformation of the methyl groups (1431 cm^{-1}) is seen at low coverages, but that feature is replaced by a new one for the symmetric mode (1375 cm^{-1}) at higher surface concentrations. Since only vibrations with dipole moments perpendicular to the surface are infrared active, we conclude that a flat geometry prevails at low coverages and that a rearrangement takes place around half saturation where the methyl group axes become perpendicular to the surface.

Formation of Surface Alkyl Groups

The carbon–halogen bond in alkyl halides adsorbed on metal surfaces can be broken easily either thermally or photolytically. The photochemistry of these systems has been studied in detail by Professor White at the University of Texas, Austin;[44] he has found that the C–X bond can be dissociated on surfaces by exposing them to ultraviolet light of lower energy than that needed in the gas phase. Thermal activation is equally effective in driving this step: the energy required to break the C–I bond on Ni(100) surfaces was measured to be less than 5 kcal/mol,[14] about the same as what has

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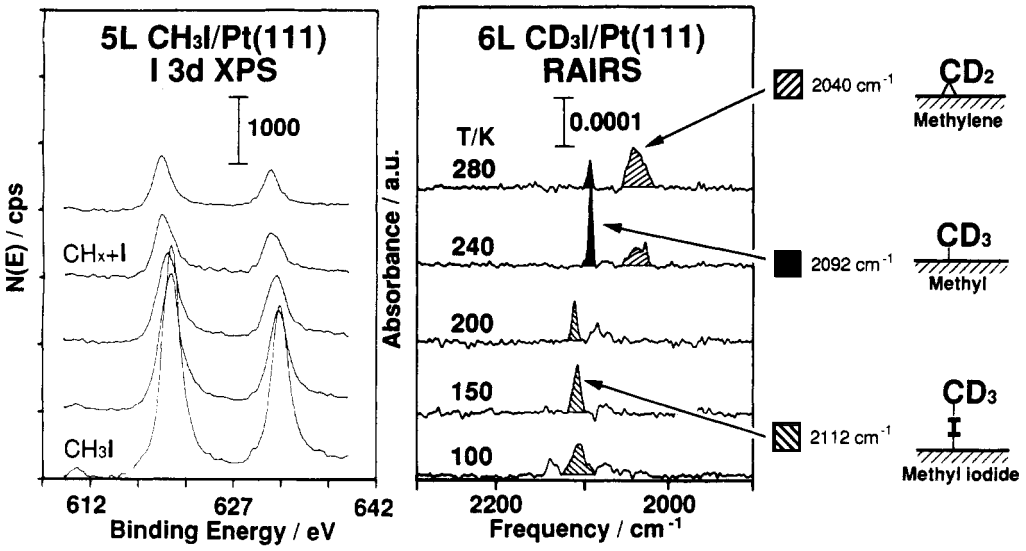

Figure 2. X-ray photoelectron (XPS, left) and reflection–absorption infrared (RAIRS, right) spectroscopic data on the thermal chemistry of methyl iodide chemisorbed on Pt(111). The XPS results illustrate the way the occurrence of the C–I bond scission was determined. Our method is based on the fact that the signal due to the I $3d_{5/2}$ electrons is quite sensitive to the chemical environment surrounding the iodine atom: the 1-eV peak shift seen between 200 and 240 K (from 620.3 to 619.3 eV) indicates that CH_3I dissociates in that temperature range. In addition, RAIRS allows for the identification of the species formed on the surface. The right panel displays vibrational data for the C–D symmetric stretching mode when starting from chemisorbed CD_3I: below 200 K one main peak is seen at 2112 cm^{-1} corresponding to methyl iodide molecularly adsorbed on the surface, but after heating to above 240 K that feature disappears completely as two new bands grow in the spectra: a sharp peak at 2092 cm^{-1}, assigned to methyl groups directly attached to the surface, and a broad feature at 2040 cm^{-1} due to methylene moieties. As the temperature is increased, the concentration of surface methyl groups goes down at the expense of the formation of methylene, until both peaks disappear completely above 300 K.

been observed in solution.[45] These reactions follow on surfaces trends similar to those in the gas phase, that is, the ease with which the bond breaks increases in going from chlorine to iodine. For instance, methyl chloride decomposes only over iron or tungsten surfaces while desorbing molecularly from silver, copper, platinum, palladium, or nickel substrates; methyl bromide does react on nickel but not on silver or platinum; and methyl iodide dissociates on all single-crystal surfaces studied to date. In addition, ethyl and propyl iodides have also been shown to dissociate on silver, copper, platinum, and nickel surfaces. It has been found that in general the early transition metals are the most active for carbon–halogen bond scission and that alkyl iodides are the best candidates for the thermal production of hydrocarbon moieties on a given metal surface.

The initial carbon–halogen bond dissociation in alkyl halides leads to the formation of chemisorbed alkyl moieties. Figure 2 exemplifies the occurrence of that reaction for the case of iodomethane adsorbed on Pt(111): the I 3d XPS data shown in the left frame indicate that the C–I bond breaks between 200 and 240 K, and the right panel displays infrared spectra showing that such a reaction produces methyl moieties on the surface.[24] Similar data were used to prove that ethyl groups are formed after ethyl iodide activation as well.[42,43]

Surface Reactivity of Alkyl Groups

Surface alkyl groups can undergo further transformations at higher temperatures by following a series of dehydrogenation, hydrogenation, H–D exchange, and polymerization reactions. Dehydrogenation steps are evidenced by the substantial desorption of hydrogen that is always detected in TPD experiments. This desorption usually takes place in several stages, which means that the hydrogen losses from those alkyl moieties may occur in a stepwise fashion and that several stable intermediates may be formed on the surface at different temperatures. For instance, the vibrational data obtained from the thermal activation of methyl iodide on Pt(111) indicate that methyl groups are converted into methylene between 240 and 280 K (Figure 2).[24] Moreover, TPD experiments have shown that while the hydrogen produced by that reaction desorbs around 330 K (in a desorption-limited step), the rest comes off above 500 K, suggesting that methylene moieties are stable over a wide range of temperatures. On Ni(100), on the other hand, hydrogen desorption is complete by 380 K, which makes the isolation of surface species other than methyl groups very difficult.[15]

The mechanism for the dehydrogenation of ethyl groups is more complex than in the case of methyl moieties because of the existence of two different carbon atoms within each molecule. H_2 TPD spectra from ethyl iodide on Pt(111) indicate that two stable species with C_2H_4 and C_2H_3 stoichiometries are formed around 270 and 300 K, respectively (Figure 3, top), and TPD data from partially labeled molecules clearly show that the first dehydrogenation step occurs at the methyl end of the ethyl groups and results in the formation of adsorbed ethylene (Figure 3, bottom).[43,46,47] Such β-hydrogen elimination is in fact well-known in organometallic chemistry and has also been shown to be the preferred dehydrogenation pathway for longer alkyl chains on surfaces.[15,31] A fraction of the olefins resulting from this reaction desorb at higher temperatures while the rest undergo further dehydrogenation in the same way as if the alkenes were dosed on the surface directly from the gas phase.[48,49] In the case of Pt(111) that last

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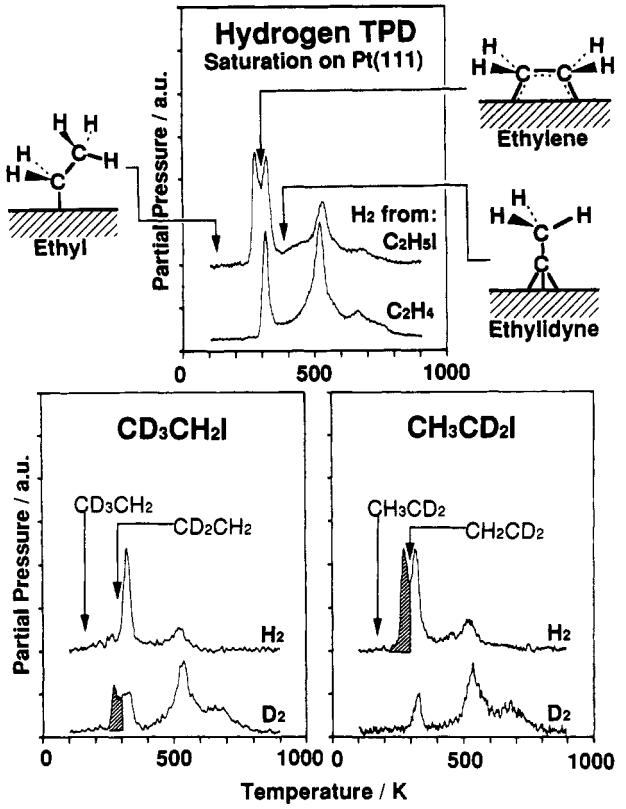

Figure 3. Hydrogen thermal programmed desorption (TPD) spectra from ethyl iodide adsorbed on Pt(111). The top frame shows that the dehydrogenation of ethyl groups takes place in three main temperature regimes: first, a hydrogen atom is lost around 270 K and chemisorbed ethylene is formed on the surface; then another hydrogen is stripped from ethylene at 300 K to form ethylidyne moieties; and finally ethylidyne dehydrogenates completely, leaving only carbon and iodine atoms on the surface. The last two steps are also seen on surfaces dosed directly with ethylene (top frame, lower trace). The two frames in the bottom half of this figure show results from experiments done with partially labeled molecules illustrating that the first dehydrogenation step occurs at the β position.

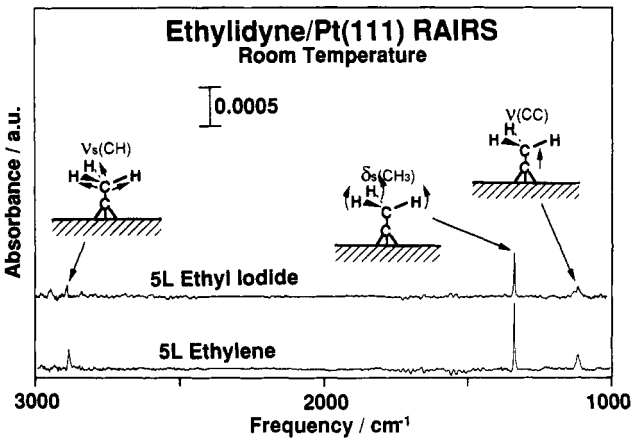

Figure 4. Reflection–absorption infrared (RAIRS) spectra for ethylidyne prepared by saturation of a Pt(111) surface with ethylene and with ethyl iodide at room temperature. Both spectra display the exact same three peaks at 1118, 1339, and 2883 cm^{-1} characteristic of ethylidyne. However, the signal intensities in the case of ethyl iodide are about half of those obtained from adsorbing ethylene because of the lower saturation coverages in the former case. There are a few other subtle differences in peak shapes between the two spectra, but the striking similarities observed point to the conclusion that iodine atoms codeposited during ethyl iodide decomposition do not alter the electronic structure of the metal surface significantly: the chemistry seen for adsorbed ethylene produced by ethyl iodide decomposition is the same as that reported from direct adsorption of gas-phase ethylene.

reaction results in the formation of alkylidyne moieties: the RAIRS spectrum for ethylidyne prepared from ethyl iodide is almost identical to that recorded from adsorbed ethylene (Figure 4). Also, since vibrations are very sensitive to local changes in electronic density, the similarity in the spectra shown in Figure 4 leads to the conclusion that iodine does not modify the metal reactivity toward hydrocarbon conversion significantly; it only blocks some of the chemisorption sites on the surface.

The thermal desorption of hydrogenation products is also quite common in these alkyl halide systems: the yield for methane formation amounts to about 75% of the methyl iodide initially chemisorbed on Pt(111)[24] and to close to 50% in the case of Ni(100),[15] and significant although smaller numbers are obtained in experiments with ethyl iodide.[22] Hydrogenation reactions proceed via the direct incorporation of hydrogen atoms into adsorbed alkyl groups as in the reductive elimination processes commonly seen in organometallic compounds. Labeling experiments have shown that the required surface hydrogen originates from the alkyl dehydrogenation steps mentioned before and that the overall reaction rate is controlled by the availability of those atoms on the surface, which is why hydrogenation products are formed only for initial alkyl halide coverages above half of saturation; at lower concentrations only dehydrogenation takes place on the surface.[22,24]

Hydrogenation reactions can be enhanced selectively by predosing the surface with hydrogen: coadsorbing small amounts of hydrogen with methyl iodide on either Ni(100) or Pt(111) surfaces results in methane yields close to 100%,[15,50,51] and over a 4-fold increase in ethane formation can be achieved by similar hydrogen treatments for ethyl iodide on Pt(111).[47] These increases in yield are also accompanied by a reduction in the energy barrier for this reaction, a change that becomes apparent by shifts in the TPD peaks to lower temperatures. One of the best examples for this behavior is provided by results from methane thermal desorption from saturation coverages of methyl iodide on Pt(111), where the main 300 K TPD peak is entirely replaced by a new feature at 275 K upon hydrogen predosing.[51]

Alkyl moieties chemisorbed on transition metal surfaces may undergo extensive H–D exchange before desorbing. For instance, TPD spectra from either CH_3CD_2I or CD_3CH_2I on Pt(111) show that about 25–30% of the ethylene that desorbs around 300 K (after β-hydrogen elimination) has experienced at least one hydrogen or deuterium substitution.[47] These results have been explained by the occurrence of a series of ethylene–ethyl interconversion steps on the surface similar to those observed for hydrogen coadsorbed with ethylene.[52–54] Also, as in hydrogenation reactions, H–D

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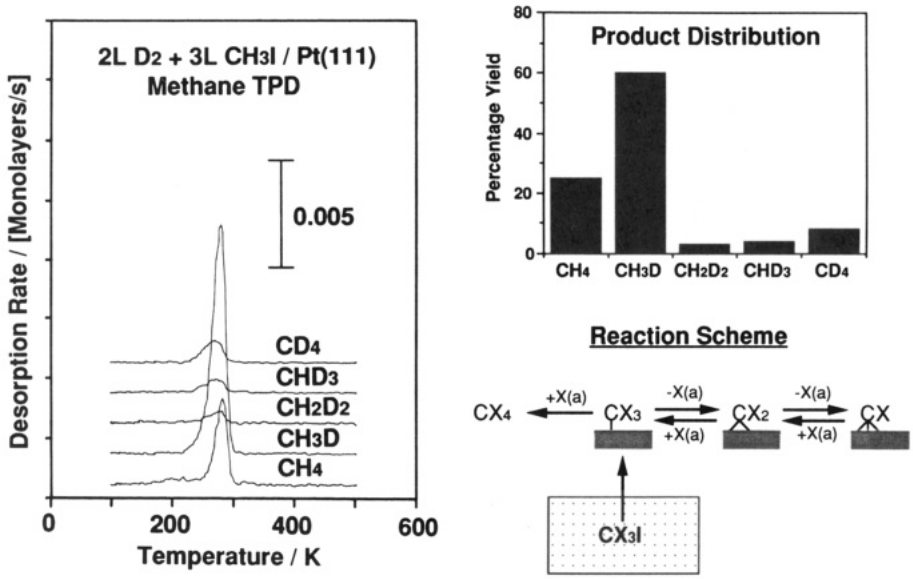

Figure 5. Methane thermal programmed desorption (TPD) data from experiments with deuterium and methyl iodide coadsorbed on Pt(111). CH_4 and CH_3D from direct reductive elimination of methyl groups by either adsorbed hydrogen or deuterium account for about 85% of all the desorbing methane, but the remaining 15% consists of molecules that have undergone one or more H–D exchange steps, and from those up to 8% correspond to CD_4 formation. In order to explain these results we propose a mechanism involving multiple and rapid interconversion steps among methyl, methylene, and methylidyne moieties on the surface.

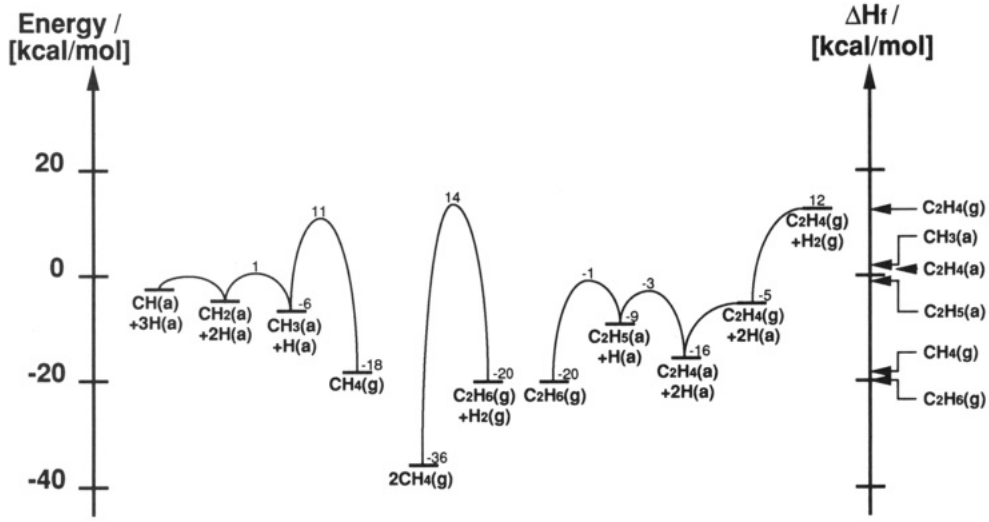

Figure 6. Energy diagram displaying data on the energetics of reactions involving C_1 and C_2 surface moieties adsorbed on Pt(111). Shown are the heats of formation for the relevant surface species (right hand side scale) as well as the kinetic activation barriers for the corresponding interconversion steps. One general conclusion derived from this diagram is that most species are about equally stable on the surface, so the direction in which the reactions involving those intermediates may go depends mostly on the energetics of surface hydrogen formation. This suggests that pressure, not temperature, may be the key parameter that controls reaction selectivites in many catalytic hydrocarbon conversion processes.

exchange on alkyl groups can be enhanced by hydrogen/deuterium predosing. The most dramatic example for this comes from our recent studies on the coadsorption of methyl iodide with deuterium over Pt(111), where we have seen that about one-quarter of the desorbing methane consists of molecules with at least one deuterium substitution and that the formation of multiply exchanged molecules is clearly favored over the formation of the monosubstituted product (Figure 5).[50,51,55] The product distributions in these TPD experiments, which are similar to those obtained from studies on the catalytic H–D exchange of methane, require the formation of at least three surface intermediates: we have proposed a mechanism that includes the formation of methyl, methylene, and methylidyne moieties where the last two species equilibrate rapidly with the hydrogen and deuterium atoms adsorbed on the surface.[51,55] To the best of our knowledge, this is the first time that reversible hydrogenation–dehydrogenation reactions have been observed in hydrocarbons adsorbed on single-crystal surfaces under vacuum, a result that proves that alkyl groups generated by the dissociation of alkyl halides can be used to model catalytic processes which take place under atmospheric conditions.

TPD experiments have also been used to estimate kinetic parameters for hydrocarbon conversion reactions on transition metals;[47,51,53,56–58] Figure 6 displays kinetic

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and thermodynamic data obtained for C_1 and C_2 moieties on Pt(111) surfaces. The heats of formation for methyl and ethyl groups on this surface are within 3 kcal/mol of each other, which means that the metal–carbon bond energies are similar in both cases (on the order of 30 kcal/mol). However, the activation barriers for the interconversion between methane and methyl groups are quite a bit higher than those for the ethane–ethyl pair, a difference of about 10 kcal/mol. On the other side of the diagram we see that the dehydrogenation of alkyl groups on platinum requires energies of about 6–8 kcal/mol, a little less for β-hydrogen elimination than for C–H dissociation in the α position. The remaining hydrocarbon fragments (methylene, methylidyne, ethylene) are almost equally stable, so their interconversion is mainly regulated by the energetics of hydrogen adsorption. This is an important conclusion for catalysis, because it implies that product selectivities may be better controlled by changing the pressures of the reactants rather than the reaction temperature.

Finally, dimerization products have been reported to form from methyl halides on Ru(100),[11] Pd(100),[19] Cu(110),[31] and foils of other transition metals,[40] as well as from ethyl and propyl moieties on Ag(111).[34,35] These carbon–carbon bond formation reactions are responsible for the production of hydrocarbons in Fischer–Tropsch catalytic processes.

Concluding Remarks

We have shown here that alkyl halides chemisorb molecularly on transition metal surfaces at low temperatures and that the scission of the carbon–halogen bond can be easily activated either thermally or photolytically to yield adsorbed alkyl moieties. The subsequent thermal chemistry of those surface intermediates is quite complex even in the most simple cases because it involves a series of hydrogenation–dehydrogenation, H–D exchange, and polymerization steps. Additionally, coadsorbing hydrogen or deuterium with alkyl halides has been shown to be a good way of simulating catalytic hydrocarbon conversion reactions under vacuum.

The use of alkyl halides as precursors for alkyl formation on surfaces is in its infancy. So far it has proven to be an exciting method for custom-making adsorbed hydrocarbon intermediates otherwise inaccessible for surface science studies, but a systematic characterization of these systems is still needed in order to learn more about the general trends in hydrocarbon chemistry on metal surfaces. Furthermore, the extension of this methodology to the synthesis of other hydrocarbon groups such as methylene, vinyl, and allyl species should also be explored.

In spite of the positive outlook given above, we should also search for alternative techniques to prepare hydrocarbon fragments on surfaces which avoid the inherent inconveniences due to the codeposition of halogen atoms in alkyl halide decomposition. The use of other radical precursors should be studied in detail. Azo compounds are excellent candidates for this purpose because they dissociate into alkyl radicals and nitrogen molecules: given that nitrogen desorbs molecularly from most transition metals, clean hydrocarbon overlayers are likely to form on the surface. The few studies done to date using this approach have provided mixed results.[59,60] Hydrocarbon radicals could also be made in the gas phase and then dosed on metal surfaces; this method is at present completely new.[61] Finally, we are investigating the possibility of delivering hydrocarbon moieties using low-energy gas-phase carbonium ions.

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