Low-Temperature Decomposition of Alkyl Iodides on Ni(100) Surfaces: Evidence for the Formation of Alkyl Free Radicals

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Previous studies have shown that alkyl iodides dissociate on metal substrates around 200 K to produce iodine atoms and alkyl moieties on the surface; here we report a new low-temperature decomposition pathway for those compounds on Ni(100) that leads to the formation of a close to 1:1 alkane–alkene mixture below 150 K. This latter reaction is proposed to occur via a mechanism where alkyl iodide dissociation results in the direct formation of free radicals. A combination of thermal desorption experiments with isotope labeling and hydrogen coadsorption was used to establish the importance of the nickel surface in the overall process and to rule out either surface disproportionation or gas-phase reactions as the source of the low-temperature products. Evidence was also obtained for a possible rearrangement of the adsorbed alkyl iodide molecules from a fat geometry into an upright configuration at high coverages, a change that would explain the ease with which the radicals formed after C–I bond scission are released into the gas phase instead of being left on the surface as adsorbed alkyl surface moieties. A comparison with other systems is also presented.

Introduction

The use of alkyl halides as precursors for the preparation of alkyl groups on transition metal surfaces under vacuum has become a common procedure in recent years.[1,2] Modern surface science studies have proven that the carbon–halide bond (the carbon–iodine bond in particular) can be easily activated on most metals at temperatures below 200 K to produce chemisorbed alkyl fragments.[1] Those surface hydrocarbon moieties can upon further heating of the sample follow a series of reactions such as hydrogenation, β-hydride elimination, disproportionation, and/or coupling depending on the initial coverages and on the nature of the metal involved.[1] It has recently become clear, however, that the adsorbed alkyl iodides can also follow other reactions on some surfaces, the nature of which remains still undetermined.[3–5]

In this paper we report some results from experiments on the thermal activation of alkyl iodides on Ni(100) related to the alternate reactions mentioned above. Earlier work has shown that at coverages below saturation the chemistry observed on that surface is similar to that reported for other metals, namely, one that involves an initial scission of the C–I bond around 160 K to form adsorbed iodine atoms and alkyl groups followed by a series of subsequent reactions of the latter moieties such as reductive and β-hydride eliminations at higher temperatures.[1,6,7] When starting with coverages close to saturation, however, new chemistry is observed on the nickel surface: here we present evidence for the production of both alkanes and alkenes through a new low-temperature pathway that we believe involves the formation of free radicals.

Experimental Section

The experiments reported here were carried out in an ultra-high-vacuum (UHV) apparatus described in previous publications.[6–9] Briefly, the stainless steel main chamber has a base pressure of less than 1×10^{-10} Torr and contains instrumentation for thermal programmed desorption (TPD), X-ray photoelectron (XPS), Auger electron (AES), ion scattering (ISS), and secondary ion mass (SIMS) spectroscopies. Thermal desorption spectra are taken using a mass spectrometer with its ionizer enclosed in the back of an energy filtering compartment (used for SIMS), the front of which has a small aperture for gas sampling. For the TPD experiments the nickel crystal is placed within 1 mm of this aperture, an arrangement that allows for the selective detection of gases desorbing from the front surface. Signals for up to 10 masses are taken simultaneously in a single TPD experiment using an interfaced computer and then deconvolved from mass spectra obtained for the different gases using the same instrument in order to extract the information corresponding to each desorbing product.[10,11] Heating rates of about 10 K/s were used in the experiments reported here.

The nickel single crystal was cut and polished in the (100) orientation by using standard procedures, mounted in a manipulator that allowed for both cooling to liquid nitrogen temperatures and heating resistively to above 1500 K, and cleaned by cycles of oxygen treatment, ion sputtering, and annealing prior to each experiment until no impurities were detected by either AES or XPS. The crystal temperature was monitored using a chromel–alumel thermocouple spot-welded onto the edge of the crystal. The normal alkyl iodides were obtained from Aldrich while the deuterated propyl iodides were purchased from MSD. They were all of a purity of 95% or better but were nevertheless distilled periodically by following several freeze–pump–thaw cycles and checked by mass spectrometry before use. All dosings were done by backfilling of the vacuum chamber. Exposures are reported in langmuirs (1 langmuir = 10^{-6} Torr·s); the pressure readings are uncorrected for differences in ion gauge sensitivity.

Results

As mentioned in the Introduction, the thermal chemistry of alkyl iodides on Ni(100) surfaces has already been investigated in some detail in recent years; the results from that work either have been or will be presented elsewhere.[4,6,9,12–15] The main conclusions from those studies relevant to the discussion to be presented in this paper are as follows: (1) The sticking coefficient of alkyl iodides on Ni(100) surfaces is approximately constant up to saturation, which is reached after exposures that go from about 3 langmuirs for methyl iodide to about 10 langmuirs for 1-pentyl iodide, and that corresponds in all cases to a coverage of about 20–30% of the number of nickel surface atoms. (2) The adsorption is molecular at liquid nitrogen temperatures, but the C–I bond of the molecules in the first layer dissociates about 160 K to yield iodine and an alkyl group which ends up adsorbed on the surface. (3) Those alkyl moieties react at higher temperatures

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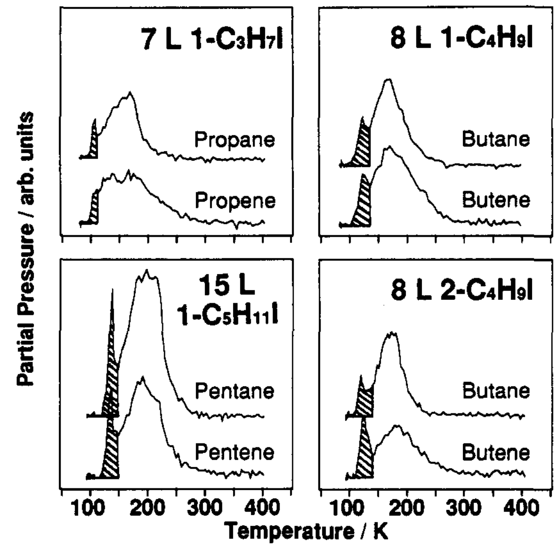

Figure 1. Alkane and alkene TPD spectra for 1-propyl (top left), 1-butyl (top right), 1-pentyl (bottom left), and 2-butyl (bottom right) iodides adsorbed on Ni(100) surfaces at 90 K. Shaded are the low-temperature peaks corresponding to the reactions being discussed in this paper. The heating rate used in these experiments was about 10 K/s.

following pathways that depend on the initial surface coverage: decomposition to hydrogen and carbon occurs almost exclusively at low surface concentrations, but reductive and hydride elimination steps dominate at higher coverages. The latter reactions, which take place between approximately 150 and 250 K and which produce a mixture of alkanes and olefins, reach a maximum in selectivity at coverages slightly below saturation, after which some additional products are detected at low temperatures as well. To illustrate this behavior, in Figure 1 we display TPD spectra for saturation coverages of 1-propyl, 1- and 2-butyl, and 1-pentyl iodides on Ni(100) where both alkane and olefin main desorption peaks are broad and centered at temperatures that go from about 160 K for the case of propyl iodide to close to 200 K for pentyl iodide. An additional sharp feature around 110–130 K is present in all those spectra (shaded area) which we believe is associated with the direct decomposition of the alkyl iodides on the surface; it is this latter peak the one we want to focus on in this paper.

The low-temperature behavior indicated above is quite general: it was observed, with some subtle differences, for all the cases studied here, namely, for 1- and 2-propyl, 1-, 2-, iso-, and *tert*-butyl, 1- and neo-pentyl, and 1-hexyl iodides. We will take the propyl iodides as representative of this family of compounds and focus our attention on their chemistry at low temperatures. Saturation for the propyl iodides corresponds to a coverage of about $\Theta = 0.3$ (as measured by XPS[15]) and is reached at exposures of about 10 langmuirs even though molecular desorption starts after about 8 langmuirs. The main desorbing products from this system are propane, propylene, and hydrogen; no coupling products such as hexane or hexene were ever detected in our experiments. The desorption of both propane and propene is seen mostly above 150 K, but a sharp peak around 115 K is also present in both TPD traces (more obviously in the one corresponding to the saturated product), a temperature a bit lower than that normally recorded for alkyl halide systems. We propose that the rate for the hydrocarbon desorption that occurs at the low temperatures is limited by the C–I bond scission step, which according to previous I $3d_{5/7}$ XPS experiments takes place mostly around 160 K,[6,15] and that the overall low-temperature reactions are associated with the direct conversion of adsorbed alkyl iodide molecules and not with the decomposition of the alkyl groups that form on the surface at higher temperatures.

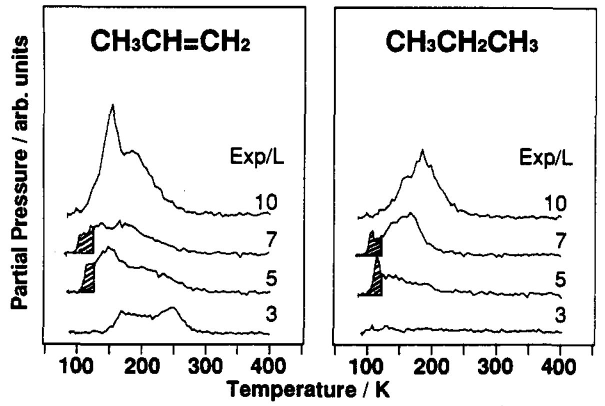

Figure 2. Propylene (left) and propane (right) TPD spectra for normal 1-propyl iodide adsorbed on Ni(100) as a function of initial exposure. Shaded again are the low-temperature features of interest in our discussion (see text).

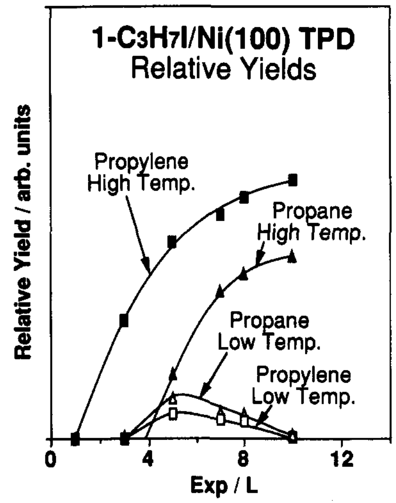

Figure 3. Relative TPD yields as a function of initial exposure for propylene and propane desorption from 1-propyl iodide decomposition on Ni(100) in both low- and high-temperature regimes.

Figure 2 displays results from a more careful study of the production of both propylene and propane from 1-propyl iodide decomposition as a function of initial exposure. The traces shown in this figure include the complete TPD spectra for each of the two compounds, but we intend to center our attention on the low-temperature shaded region, where a peak grows beginning at exposures around 4 langmuirs, reaches a maximum in intensity around 5 langmuirs, and disappears by 10 langmuirs (at doses slightly above those required to start building up a second layer). This behavior is better illustrated in Figure 3, which displays the relative yields for the low- and high-temperature peaks for both propane and propylene as a function of initial exposure. The data indicate that the low-temperature chemistry is mediated by the nickel surface and that it involves alkyl iodides chemisorbed in the first layer, because those reactions shut down in the presence of a second condensed layer.

To help elucidate the mechanism for the low-temperature reactions it is useful to note that, while the formation of propylene only requires the elimination of hydrogen and iodine atoms from propyl the iodide molecule, propane production requires the incorporation of an additional hydrogen. In order to identify the source of this extra hydrogen, TPD experiments were performed with compounds partially labeled with deuterium. Figure 4 shows both propylene and propane TPD spectra for 5 langmuirs $CH_3CH_2CD_2I$ (upper left), 5 langmuirs $CH_3CD_2CH_2I$ (upper right), 6 langmuirs CD_3CHICD_3 (lower left), and 6 langmuirs CD_3CDICD_3 (lower right) adsorbed on Ni(100) surfaces. The interesting fact to notice here is that the propane that desorbs at low temperatures is mostly the result of the incorporation of normal hydrogen into the original propyl group, in contrast with the

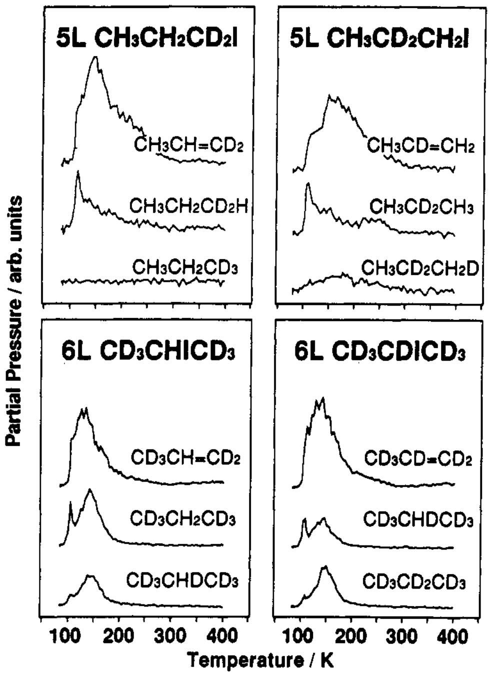

Figure 4. Propylene and propane TPD spectra from Ni(100) surfaces dosed with 5 langmuirs $CH_3CH_2CD_2I$ (top left), 5 langmuirs $CH_3CD_2CH_2I$ (top right), 6 langmuirs CD_3CHICD_3 (bottom left), and 6 langmuirs CD_3CDICD_3 (bottom right) at 90 K.

behavior seen in the high-temperature regime, where this is not always the case. Indeed, the propyl groups that result from C–I bond dissociation at the higher temperatures undergo a reductive elimination step with the hydrogen atoms available on the surface, which in the case of the 1-propyl iodide labeled in the first carbon (the one closest to the iodine atom) consist only of normal H (only $CH_3CH_2CD_2H$ desorbs from the surface), but which in the experiments with the other compounds also include some deuterium produced by the β-D elimination reactions. The same surface hydrogen incorporation does not take place at low temperatures, so while $CH_3CD_2CH_2I$ decomposition leads to the production of both $CH_3CD_2CH_3$ and $CH_3CD_2CH_2D$ at high temperatures, it only yields $CH_3CD_2CH_3$ at low temperatures, and, in the same way, very little CD_3CHDCD_3 and $CD_3CD_2CD_3$ desorb from CD_3CHICD_3 and CD_3CDICD_3, respectively, in the low-temperature regime.

Since the results presented above indicate that the extra hydrogen required in the formation of alkanes does not originate from other alkyl iodide molecules, we turn our attention now to the search of alternative sources for such atoms. Figure 5 displays results from TPD experiments designed to address this point: one done under vacuum after dosing propyl iodide alone on the nickel surface (left), another two recorded for the same system but while maintaining fixed pressures of deuterium (center) or deuterated water (not shown) gases during the TPD experiment, and a fourth where a small amount of deuterium was dosed on the surface prior to propyl iodide adsorption (right). Having either deuterium or deuterated water vapor present in the background of the vacuum chamber during the experience does not alter the chemistry observed in this system: no additional reactions seem to take place either with D_2 or D_2O molecules in the gas phase or with D atoms near the mass spectrometer ionizer, and, in addition, no deuterium adsorbs on the surface after such large doses of propyl iodide. In fact, the possibility of adsorbing additional hydrogen (deuterium) on the surface after dosing the propyl iodide was tested more carefully by titrating the available surface sites with deuterium. The TPD data displayed in Figure 6, obtained after dosing variable amounts of propyl iodide first and 2 langmuirs D_2 afterwards, shows that while the desorption of H_2 (which originates from propyl iodide decomposition) increases substantially with increasing initial propyl iodide exposure (and develops a low-temperature feature that dominates at high coverages), both HD and D_2 spectra only display single peaks around 340–360 K. The inset in Figure 6 shows that there is an almost linear decrease in deuterium uptake as a function of propyl iodide predose until all adsorption surface sites are blocked, which occurs after an exposure of only 2 langmuirs propyl iodide (about one-fifth of that required for monolayer saturation). This result can be explained by assuming that at low coverages the alkyl iodide adsorbs in an initial geometry with the alkyl chains parallel or close to parallel to the surface (occupying a large surface area) which changes to a more vertical configuration with increasing doses; this phenomena has in fact been observed directly by reflection–absorption infrared experiments in similar systems.[17–19]

When small amounts of deuterium are adsorbed on the nickel surface prior to 1-propyl iodide dosing (Figure 5, right), the yield for the production of $CH_3CH_2CH_2D$ via the reductive elimination of the alkyl groups with deuterium is enhanced at high temperatures, but the behavior at low temperatures is not modified: no deuterated propane is observed in this temperature regime. In experiments with propyl iodides with β-deuteriums normal hydrogen incorporation is still the main reaction observed below 150 K, but a small amount of deuteration is detected as well; still,

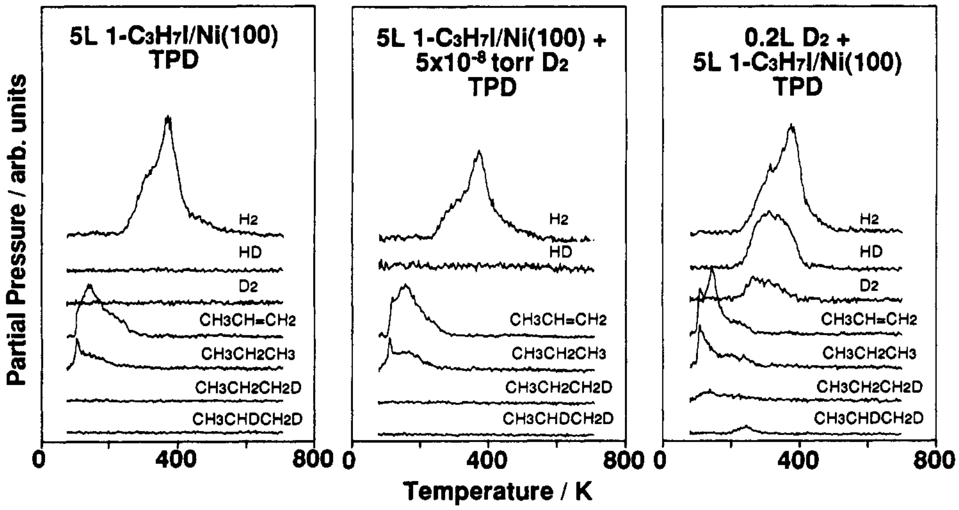

Figure 5. H_2, HD, D_2, propylene, and normal, *-1-d*, and propane-*1,2,d*$_2$ TPD spectra for 5 langmuirs of normal 1-propyl iodide on a clean Ni(100) surface both under vacuum (left) and while keeping a 5 × 10^{-8} Torr pressure of deuterium in the chamber (center), and on a surface predosed with 0.2 langmuirs of deuterium (right).

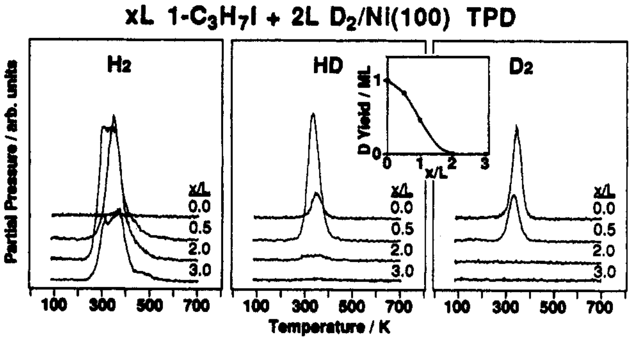

Figure 6. H_2, HD, and D_2 TPD spectra from Ni(100) surfaces dosed sequentially with different exposures of normal propyl iodide and 2 langmuirs D_2 at 90 K. The inset displays the total deuterium yield (deuterium atoms in HD and D_2) as a function of initial propyl iodide exposure (the value for 0 langmuirs C_3H_7I was corrected by the small background hydrogen adsorption that always takes place in vacuum chambers).

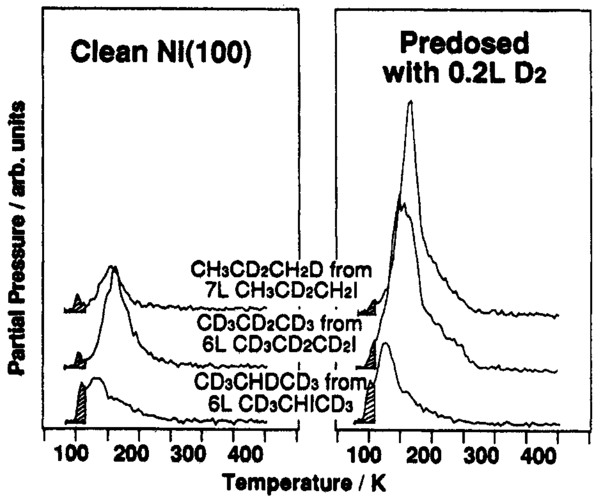

Figure 7. Propane TPD spectra from deuterium incorporation into isotopically labeled propyl iodides on clean (left) and deuterium predosed (right) Ni(100) surfaces. The low-temperature peaks relevant to this paper are again shaded in this figure.

the amounts of both hydrogenated and deuterated propanes produced at low temperature do not change with deuterium surface predosing as in the high-temperature main regime (Figure 7). It should be pointed out that only small coverages of predosed deuterium (0.2 langmuirs, which corresponds to coverages of about 20% of saturation) were used in this experiments because larger predoses modify the overall surface chemistry, increasing the yield for alkane formation and shifting the maxima of the low-temperature sharp peak from 115 to about 130 K.[16]

Finally, coadsorption experiments with methyl iodide were performed in an attempt to use methyl groups either as a source or as a scavenger of surface hydrogen atoms (Figure 8). As in the other cases studied to date on Ni(100) surfaces, no coupling products were detected here: only hydrogen, methane, propane, propylene, and molecular methyl and propyl iodides desorb in these experiments. When β-labeled propyl iodide (5 langmuirs $CH_3CD_2CH_2I$) is dosed first, the very little methyl iodide that adsorbs later desorbs either molecularly at 135 K (not shown) or as CH_4 around 140 K; no CH_3D was detected at all even though propylene formation, which requires the removal of a deuterium atom, occurs at temperatures as low as 110 K. This indicates that the deuterium byproduct of the low-temperature elimination step is not deposited on the surface and therefore suggests that the reaction occurs elsewhere. Moreover, the low-temperature propane formed in this case is again the result of the addition of normal hydrogen, not deuterium, into the propyl moieties, as opposed to what is seen at higher temperatures, where both $CH_3CD_2CH_3$ and $CH_3CD_2CH_2D$ are produced. In experiments where the order of adsorption was reversed, namely, when methyl iodide was dosed first, there was a much larger production of methane, of both normal CH_4 and monodeuterated CH_3D, but only above 170 K, and, once more, only $CH_3CD_2CH_3$, not $CH_3CD_2CH_2D$, was produced around 110 K. Low-temperature methane formation from methyl iodide coadsorbed with hydrogen (or deuterium) is possible under the right circumstances,[4,14] so the absence of any features in the CH_3D TPD spectra from the coadsorption experiments below 150 K argues for the lack of deuterium atoms on the surface.

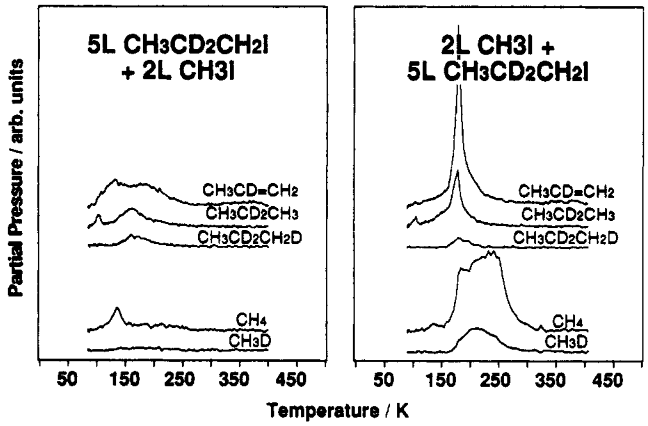

Figure 8. $CH_3CD{=}CH_2$, $CH_3CD_2CH_3$, $CH_3CD_2CH_2D$, CH_4, and CH_3D TPD spectra for 5 langmuirs $CH_3CD_2CH_2I$ and 2 langmuirs CH_3I coadsorbed on Ni(100), dosed in that order (left) or in the reverse sequence (right).

Discussion

Alkyl iodides follow on Ni(100) a thermal chemistry that is in general similar to that observed on other metal surfaces, namely, they undergo a C–I bond scission step that results in the formation of surface alkyl groups which then react to form alkanes, alkenes, hydrogen, and carbon.[1,6,7] There is, however, a new set of reactions that opens up on Ni(100) at low temperatures, below 150 K, around saturation coverages; it is the nature of these reactions that we want to address below.

The first observation of relevance that derives from the experiments reported here is the fact that the alkyl iodide low-temperature chemistry seen on Ni(100) is quite general; the thermal activation of any alkyl iodide with more than two carbons results in the appearance of features in the alkane and alkene TPD traces around 120 K. The peak shapes and yields for both products are in many cases quite similar (perhaps alkane formation is slightly favored in some cases), so the two molecules are most likely produced by reactions kinetically limited by the formation of a common intermediate. Some significant differences are nevertheless observed for iodides with branched hydrocarbon moieties: the yield for isobutane desorption from either 1- or 2-iodo-2-methylpropane, for instance, is quite low, less than 10% of that of isobutene (data not shown). This latter effect is also seen in the high-temperature chemistry of the corresponding surface alkyl moieties and is probably due to either steric or electronic effects (to the relative stability of the alkyl radicals that may form during the reaction).

The desorption observed in our experiments below 150 K must originate from the direct conversion of adsorbed alkyl iodides, not alkyl groups, on the nickel surface, because these latter species are produced at lower coverages and react at higher temperatures. The change in chemical behavior detected at the close to saturation surface concentrations must be directly or indirectly induced by some crowding of the surface and is perhaps related to some type of adsorbate–adsorbate interactions. Also, these new low-temperature reactions are related to alkyl iodides adsorbed on clean nickel surfaces and not induced by coadsorbed hydrogen as in the situation observed previously for methyl iodide.[4,14]

The low-temperature chemistry seen for the alkyl iodides is surface mediated, since the yield for the desorbing products in this temperature regime goes through a maximum at a coverage of around 50% of a monolayer and becomes zero once a multilayer starts to condense on the substrate. The coadsorption experiments reported in Figure 8, however, argue for the low-temperature dehydrogenation (β-hydride elimination) step taking place some place other than on the nickel surface, because if that particular reaction were to be mediated by the Ni(100), the deuterium atoms produced by the decomposition of $CH_3CD_2CH_2I$ should end up on that surface and should incorporate into the methyl groups coadsorbed with the propyl iodide. The results displayed in Figure 8 show that this is in fact not the case: the methyl iodide adsorbed on the Ni(100) surface after β-labeled propyl iodide dosing produces only normal methane, CH_4. Also methane desorbs around 140 K, a temperature lower than that required for β-D elimination from surface propyl groups but not from propyl iodide, which means that no deuterium is provided to the surface by the latter reaction.

A question that needs to be answered in order to understand the mechanism by which the overall low-temperature reaction occurs is that referring to the source of the extra hydrogen atom required for the formation of alkane molecules out of the initial alkyl iodides. One of the most common sources of such hydrogen both in organometallic compounds and in gas- and liquid-phase radicals (and even on surfaces at higher temperatures) is another hydrocarbon fragment; the hydrogen transfer in those cases takes place either directly via a bimolecular concerted disproportionation reaction, or mediated by the metal after a previous dehydrogenation step.[1,20,21] Mechanisms such as these are capable of simultaneously explaining the formation of the alkane and the alkene and also of justifying the similar kinetics and comparable yields observed for the formation of the two products. Unfortunately, a direct disproportionation mechanism cannot explain the low-temperature chemistry reported here, since significant quantities of propanes with at least one normal H atom do form from activation of fully deuterated propyl iodides (Figure 4). Some deuterium incorporation is seen into the propyl groups of molecules with β-deuteriums (Figure 7), indicating that at least part of the hydrogens (deuteriums) in the resulting propane comes from other propyl iodide molecules, but since the main product in those cases is still the hydrogenated propane, the transfer of such atoms must still be mediated by a solid surface.

The role of coadsorbed hydrogen in the low-temperature hydrogenation step was studied by performing experiments on deuterium predosed Ni(100) surfaces. The only low-temperature propane that results from the thermal activation of normal 1-propyl iodide is C_3H_8 regardless of if deuterium is present on the surface or not, so the incorporation of surface hydrogen (deuterium) must not be important below 150 K (Figure 5). A small amount of deuterium incorporation is indeed observed when starting with deuterated propyl iodides, but the relative yields for the deuterated and the hydrogenated propanes produced in those cases are also unaffected by the presence of surface deuterium (Figure 7). The low level of deuterium preexposure used in these experiments could in principle limit the validity of the conclusion reached above because of the unavoidable coadsorption of normal hydrogen from the background, but the fact that some deuterated propane does desorb at higher temperatures indicates that there is enough deuterium on the surface to induce surface deuteration if this were to be a feasible step. We therefore conclude that the extra hydrogen in the alkane produced at low temperatures does not originate from the nickel surface either.

It is quite difficult to envision the mechanism by which the low-temperature reactions do occur in these systems. Additional propyl iodide TPD experiments were done in the presence of a background pressures of deuterium and D_2O in order to test the possibility of the occurrence of some gas-phase reactions either with molecular hydrogen or water near the surface or with atomic hydrogen near the mass spectrometer ionizer. The negative results obtained in those cases (the two left frames in Figure 5 are almost identical) lead us to rule out these possibilities as well and to propose a scheme where the low-temperature C–I bond breaking that takes place at high coverages results in the formation of free alkyl radicals in the gas phase which then react elsewhere, probably on the walls of the vacuum chamber, to produce the alkanes and alkenes observed in the TPD experiments. This possibility is quite reasonable from the thermodynamic point of view, since the initial reaction is close to isoenergetic: the breaking of the C–I bond requires an energy similar to that released by the formation of the Ni–I bond, on the other of 60 kcal/mol.[9,22] Kinetically the formation of free radicals must compete with the possible adsorption of the resulting hydrocarbon fragments on the surface, a much more exothermic reaction that indeed dominates at low coverages but that may be inhibited near saturation because the surface may be too crowded to provide the space required for alkyl adsorption. In this respect it is relevant to remember that the titration experiments reported in Figure 6 indicate that the nickel surface is already completely covered after propyl iodide doses of only about 2 langmuirs. Also, the upright configuration of the adsorbed molecules at high coverages is more likely to induce the ejection of the alkyl radicals into the gas phase once the C–I bond is broken. Further support for our hypothesis comes from the observation that the low-temperature reaction channel shuts down when a second layer is condensed on top of the first monolayer, presumably because such layer impedes the release of the free radicals into the vacuum and forces them to recombine on the nickel surface instead. On the other hand, the hypothesis presented above neither provides a satisfactory explanation for the similar yields observed for the alkane and the alkene other than this may be fortuitous, nor does it explain the lack of at least some deuterium incorporation in the alkane produced in the presence of background D_2 or D_2O pressures in the chamber. It would be desirable to detect the free radicals that suppose to form in these reactions directly in the gas phase, but this is quite difficult and requires a different experimental apparatus:[5,23] our present setup does not allow for the direct line-of-sight mass spectrometric detection of molecules desorbing from the single-crystal surface, but, for that same reason, the conversion of free radicals into more stable species on other surfaces before detection is to be expected.

Even though the formation of alkyl free radicals from surface reactions is not common, there is already some precedent for it. Specifically, Lin et al. have recently reported some evidence for the formation of such radicals from alkyl iodides on Cu(111) surfaces.[5] The comparison between their system and ours is particularly relevant, since copper and nickel are adjacent elements in the periodic table, and since radical formation has in both cases been only seen for heavy alkyl iodides, at quite low temperatures, and at coverages close to saturation. In the copper case the main evidence for radical formation comes from the relative yields observed for the products formed from disproportionation and coupling reactions, which are close to those obtained in experiments with free radicals. Since both those reactions involve bimolecular steps, however, the radicals formed on the surface must be trapped in a weakly physisorbed state if they are to follow the required binary collisions; this does seem to occur on copper, but definitely not on nickel, where coupling products were never observed. Otherwise, the energetics for radical formation is expected to be similar on nickel and copper surfaces, since both alkyl iodides and atomic iodine atoms display comparable heats of adsorption on both metals.

Conclusions

The results reported here indicate that in addition to the well-known thermal chemistry that alkyl iodides follow on metal surfaces, which involves the scission of the C–I bond and the concurrent formation of surface alkyl moieties, a second set of reactions occurs at high coverages on Ni(100) surfaces which produces alkane and alkene molecules in a close to 1:1 relation. This new pathway takes place at very low temperatures, below 150 K, and most probably involves the direct decomposition of adsorbed alkyl iodide to alkyl free radicals. Our evidence for this can be summarized as follows: (1) the reaction is surface mediated and inhibited by the presence of a second physisorbed alkyl iodide layer; (2) the hydrogen atoms that incorporate into the alkyl groups to produce the corresponding alkanes do not originate from any direct alkyl iodide disproportionation reaction (as shown by isotope labelling experiments), neither they come from the nickel surface (no predosed deuterium is incorporated in the gaseous products); (3) alkenes are formed by the elimination of a hydrogen from the beta position of the original alkyl moieties, but that hydrogen does not adsorb on the nickel surface either; and (4) hydrogen incorporation does not occur in the gas phase. All this leads us to propose a scheme where free radicals are released into the gas phase and subsequently converted to alkanes and alkenes on the walls of the vacuum system. Radical formation can be justified both thermodynamically, since the reaction is about isoenergetic, and kinetically, because the surface is crowded and the alkyl iodides are most likely adsorbed with a perpendicular geometry.

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