Thermal Reactions of Alkyl Iodides on Ni(100) Single Crystal Surfaces

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Abstract: The chemistry of 1-iodopropane, 1-iodobutane, 2-iodobutane, 1-iodo-2-methylpropane, 2-iodo-2-methylpropane, 1-iodopentane, and 1-iodohexane on Ni(100) surfaces has been studied by using temperature-programmed desorption and X-ray photoelectron spectroscopy. Below 100 K all the compounds adsorb molecularly through the iodine atom. The hydrocarbon chain orients parallel to the surface at first, but flips as the coverage increases, and becomes perpendicular to the surface at saturation. The C–I bond dissociates between 120 and 180 K to yield the corresponding alkyl fragment on the surface. At higher temperatures the alkyl groups decompose further, directly to carbon and hydrogen at low coverages (below half-saturation), but mainly to a mixture of alkanes and alkenes at saturation. The change in the ratio between alkane and alkene production was examined with respect to both the degree of substitution and the length of the carbon chain. It was found that the β-hydride elimination that yields the alkenes is favored over the reductive elimination responsible for the alkane formation in alkyl species with a large number of β-hydrogens, even in the presence of coadsorbed hydrogen on the surface. On the other hand, the hydrogenation steps were seen to dominate in the coadsorbed systems for alkyl species with a small number of β-hydrogen atoms. An increase in chain length has the effect of decreasing the alkene-to-alkane ratio further.

1. Introduction

The thermal chemistry of alkyl iodides on metal surfaces has already been studied in some detail by both us and others.[1] It has been shown that on most transition metals the initial activation of the C–I bond generates alkyl fragments and iodine atoms on the surface. This makes these systems quite useful, because the resulting alkyl fragments can be used to study the reactions involved in hydrocarbon conversion processes such as Fisher–Tropsch synthesis and alkane activation.[2,3] Our recent studies on Ni(100) show that small alkyl fragments undergo both hydrogenation and dehydrogenation reactions simultaneously to form alkanes and alkenes, respectively;[4–6] the alkene is formed through a β-hydride elimination step, while the alkane is generated via the reductive elimination of alkyl species with hydrogen atoms originating from either adsorption of background gases or the β-hydride elimination step. The latter reaction is favored by the presence of coadsorbed surface hydrogen even under ultra-high-vacuum (UHV) conditions.[7,8]

As part of our continuing studies on the chemistry of alkyl iodides on metal surfaces, here we report results from temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) studies on the chemistry of C_3 to C_6 alkyl iodides on Ni(100) surfaces. The adsorptions of 1-iodopropane, 1-iodobutane, 2-iodobutane, 1-iodo-2-methylpropane, 2-iodo-2-methylpropane, 1-iodopentane, and 1-iodohexane were all found to be molecular below 100 K, but decomposition was seen to start around 120 K via the cleavage of the C–I bond to form alkyl groups and iodine atoms on the surface. The alkyl fragments were found to subsequently react via β-hydride and reductive elimination steps to alkenes and alkanes, respectively. The relative reactivity toward alkene and alkane production was found to depend both on the degree of substitution and on the length of the hydrocarbon chain. It was seen that the alkene-to-alkane ratio increases with increasing number of β-hydrogens in the alkyl group, and decreases with increasing carbon chain length for alkyl species with the same number of β-hydrogen atoms.

2. Experimental Section

The experiments reported here were performed in an ultra-high-vacuum (UHV) chamber described in detail elsewhere.[4,9] This chamber is evacuated by a turbomolecular pump to a base pressure of about 1×10^{-10} Torr, and is equipped with instrumentation for temperature-programmed desorption (TPD) and X-ray photoelectron (XPS), static secondary ion mass (SSIMS), Auger electron (AES), and ion scattering (ISS) spectroscopies. Temperature-programmed desorption spectra were obtained by recording the mass spectrometry signals of up to 12 different masses simultaneously in a single experiment by using an interfaced computer. A heating rate of about 10 K/s was used in these TPD runs. The TPD signal intensities are reported in arbitrary units, but the different panels within each figure can still be compared directly, since they were plotted using the same scale. Also, those signals were calibrated by using reference compounds in order to calculate absolute product yields.[4–6] XPS spectra were taken by using an aluminum anode X-ray source and a hemispherical electron energy analyzer of 50 mm radius set at a constant pass energy of 50 eV, which corresponds to a resolution of about 1.2 eV full width at half-maximum. The energy scale was calibrated using binding energy values for the Pt $4f_{7/2}$ and Cu $2p_{3/2}$ signals of 70.9 and 932.4 eV, respectively.[9]

The nickel single crystal was cut and polished in the (100) orientation using standard procedures, and mounted in a manipulator capable of cooling to liquid nitrogen temperatures and resistively heating to up to 1300 K. The temperature of the sample was measured with a chromel–alumel thermocouple spot-welded to the back of the crystal. Cleaning of the crystal was done by oxygen treatment and argon ion sputtering

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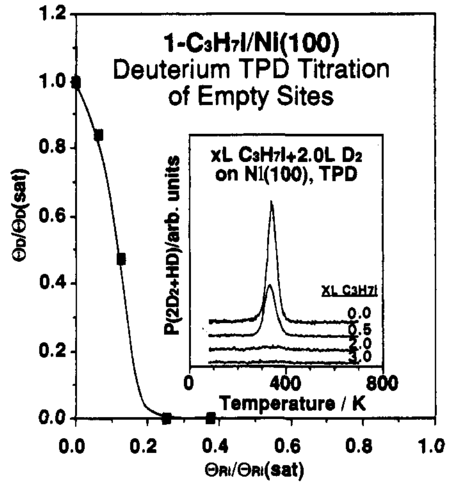

Figure 1. Deuterium TPD titration of surface sites as a function of propyl iodide coverage. The inset shows the TPD traces for the total deuterium obtained after sequentially dosing different initial amounts of propyl iodide and 2.0 L D_2, and the main frame displays the deuterium total yields obtained by integration of the TPD traces.

cycles followed by annealing to about 1300 K until no impurities were detected by either AES or XPS.

All the alkyl iodides were purchased from Aldrich and were subjected to several freeze−pump−thaw cycles before introduction into the vacuum chamber. Their purity was checked periodically by mass spectrometry. Surface exposures are reported in langmuirs (1 L = 1 × 10^{-6} Torrs); the pressure readings were not corrected for differences in ion gauge sensitivities.

3. Results

Previous experiments have shown that the adsorption of alkyl iodides is molecular on most transition metal surfaces at low temperatures (<100 K).[1,4,5] Additional evidence indicates that the chemisorption geometry of those molecules changes with coverage, from having the alkyl chains flat on the surface at low coverages, to a packed and standing up configuration at saturation.[10−12] As an example of the data obtained here to support this statement, Figure 1 shows results from a deuterium TPD titration experiment as a function of propyl iodide precoverage. There, it can be seen that the amount of deuterium that adsorbs on the Ni(100) surface is completely suppressed after adsorbing as little as 20% of saturation of C_3H_7I and that no measurable deuterium signal is visible after dosing 2.0 L C_3H_7I (as shown in the inset of Figure 1), even though saturation occurs at an exposure of 8.0 L C_3H_7I. This implies that the propyl iodide molecules cover a large area, suggesting that they lie flat on the surface. At the other end, an indication that the alkyl iodide molecules are stacked in an upright position at saturation comes from the fact that their saturation coverage depends little on the nature of the alkyl chain. To illustrate this, Figure 2 displays results from I 3d XPS measurements from saturated monolayers of iodomethane (CH_3I), iodoethane (C_2H_5I), 1-iodopropane (C_3H_7I), 1-iodobutane (C_4H_9I), and 1-iodopentane ($C_5H_{11}I$) on Ni(100), first adsorbed at 90 K and then annealed to 180 K to desorb any condensed multilayers. As highlighted in the inset of Figure 2, the coverages determined by the XPS peak areas are quite similar, within experimental error, for the monolayers of all these alkyl iodides; they correspond to a saturation coverage of about a quarter of a monolayer. In fact, the coverages for methyl and ethyl iodides are slightly lower than the rest, perhaps because some molecular desorption takes place from the saturated monolayer in those cases.

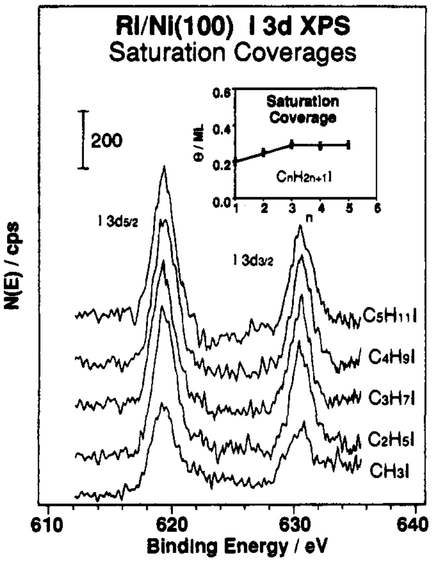

Figure 2. Iodine 3d XPS spectra from saturated monolayers of iodomethane, iodoethane, 1-iodopropane, 1-iodobutane, and 1-iodopentane prepared by first dosing a multilayer of the alkyl iodides (10.0 L CH_3I, 15.0 L C_2H_5I, 15.0 L C_3H_7I, 20.0 L C_4H_9I, and 20.0 L $C_5H_{11}I$) on Ni(100) at 90 K and then annealing to 180 K to desorb any condensed layers. The inset summarizes the corresponding iodine coverages as a function of chain length.

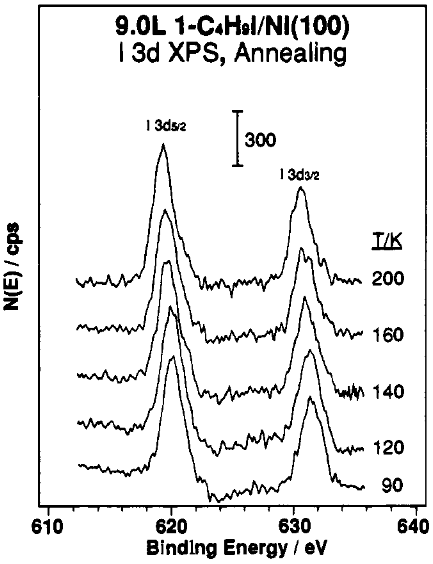

Figure 3. Iodine 3d spectra from 9.0 L 1-iodobutane dosed on Ni(100) at 90 K and annealed to the indicated temperatures.

The thermal activation of chemisorbed alkyl iodides has been shown to initially lead to the scission of the C−I bond and to the formation of alkyl groups on most transition metals.[1] To gain information about the energetics of this initial C−I bond dissociation step on Ni(100), I 3d XPS spectra were taken for the different adsorbed alkyl iodides as a function of annealing temperature. As an example of the type of data obtained from these experiments, Figure 3 displays an XPS series from 9.0 L 1-iodobutane first adsorbed on Ni(100) at 90 K and then annealed to the indicated temperatures. As for all the other alkyl iodides, neither the area nor the shape of the I 3d XPS peaks was seen to change significantly by annealing of the sample. The binding energies, on the other hand, shift from

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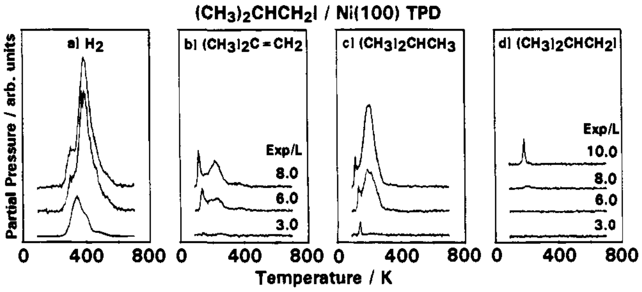

Figure 4. Hydrogen (a), isobutene (b), isobutane (c), and molecular (d) TPD spectra from 1-iodo-2-methylpropane adsorbed on Ni(100) as a function of initial exposure. In all cases the dosing was done at 90 K, and a heating rate of about 10 K/s was used.

about 620.1 and 631.6 eV at 90 K to 619.6 and 631.0 eV at 200 K. It has been shown previously that an I $3d_{5/2}$ binding energy of 620.1 eV is characteristic of iodine bonded to alkyl groups, and that a value of 619.6 eV corresponds to surface iodine instead.[5,9] The changes observed in these experiments are therefore indicative of the fact that the dissociation of the C−I bond in alkyl iodides on Ni(100) surfaces takes place below 200 K. This is consistent with the results reported for other surfaces.[9,13−16]

The subsequent thermal chemistry of the chemisorbed alkyl groups resulting from alkyl iodide activation on Ni(100) was determined by TPD studies such as those summarized in Figure 4 for 1-iodo-2-methylpropane (isobutyl iodide). Only hydrogen, isobutene, isobutane, and molecular desorption was seen in this case. Analogous results were obtained for the other compounds; no cracking or recombinatory products were ever detected in these systems. Figure 4a shows that at low coverages (less than 3.0 L) all the hydrogen produced from the decomposition of the isobutyl groups desorbs in one peak about 340 K. However, as the initial exposure is increased, the TPD trace broadens, splitting into a main peak about 390 K and a low-temperature shoulder around 310 K. The high temperature at which most of this desorption occurs suggests that at high coverages the kinetics for the H_2 desorption may be limited by the decomposition of hydrocarbon surface species, and not by hydrogen atom recombination as in the low coverage limit. Also, the overall hydrogen yield decreases by about 70% when going from 3.0 to 8.0 L, indicating that total decomposition of the alkyl species competes with other hydrocarbon-forming reactions at high coverages.

Figure 4b summarizes the coverage dependence of the isobutene TPD from 1-iodo-2-methylpropane on Ni(100). No alkene formation was detected after low doses; only above 3.0 L was some isobutene seen to desorb from the surface. This isobutene desorbs in two temperature regimes, which in the 6.0 L spectra appear as a sharp peak at 135 K and a broad feature centered about 215 K. At even higher exposures (8.0 L), the low-temperature peak shifts to about 115 K but the high temperature feature stays in about the same place, suggesting first-order kinetics. In fact, isobutene molecular TPD results from experiments with isobutene adsorbed on clean Ni(100) surfaces indicate that the alkene desorption occurs around 135 K, thus indicating that the shape of the isobutene TPD trace from 1-iodo-2-methylpropane is controlled by the kinetics of the surface decomposition reaction. Finally, the total isobutene yield increases by about a factor of 2 as the 1-iodo-2-methylpropane exposure increases from 6.0 to 8.0 L.

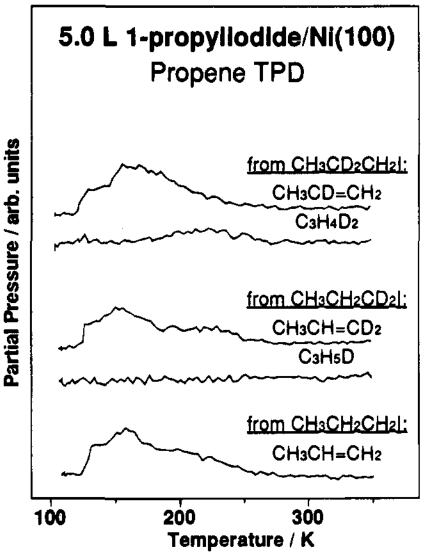

Figure 5. Propene (C_3H_6, C_3H_5D, and $C_3H_4D_2$) TPD spectra from Ni(100) surfaces dosed with 5.0 L $CH_3CH_2CH_2I$, $CH_3CH_2CD_2I$, and $CH_3CD_2CH_2I$ at 90 K.

The corresponding TPD spectra for the isobutane desorption are shown in Figure 4c. As in the case of isobutene, very little isobutane is detected at low coverages (below 3.0 L). A sharp peak at 135 K and a second broad one at 205 K develop after a 6.0 L exposure. The total isobutane yield increases at higher coverages, up to about a factor of 4 at saturation. The sharp peak shifts to 115 K, while the shape and position of the broad feature stays about the same, as in the case of the alkene.

Finally, Figure 4d displays the TPD traces corresponding to the molecular desorption of 1-iodo-2-methylpropane. No molecular desorption takes place below 8.0 L, only at that point a small feature starts to grow at about 180 K. The molecular desorption peak sharpens with increasing exposure, and grows indefinitely. Given that it also displays zero-order kinetics, it is assumed to correspond to the desorption of physisorbed 1-iodo-2-methylpropane. By using a leading edge analysis method,[17] the sublimation energy of this condensed layer was estimated to be about 9 ± 3 kcal/mol. All other physisorbed alkyl iodides display about the same sublimation energy, except for iodohexane, which yielded a value of about 12 ± 2 kcal/mol. These values match reasonably well those reported in literature.[18]

In order to determine the mechanism for the formation of alkenes from alkyl decomposition, additional TPD experiments were performed with partially deuterated alkyl iodides. The TPD spectra obtained for propene desorption from $CH_3CH_2CH_2I$, $CH_3CH_2CD_2I$, and $CH_3CD_2CH_2I$ are summarized in Figure 5. As can be seen in that figure, only one kind of propene is produced in each case, namely, $CH_3CH{=}CH_2$, $CH_3CH{=}CD_2$, and $CH_3CD{=}CH_2$, respectively. Since no C_3H_5D was seen to desorb from $CH_3CH_2CD_2I$, and no significant $C_3H_4D_2$ was produced from $CH_3CD_2CH_2I$, it is concluded that the propenes in these systems are formed by a β-hydride (or β-deuteride) elimination from the original alkyl moiety. In addition, the $CH_3CD{=}CH_2$ resulting from $CH_3CD_2CH_2I$ decomposition desorbs at about 165 K, a slightly higher temperature than those for $CH_3CH{=}CH_2$ and $CH_3CH{=}CD_2$ desorption (which peak at a 150 K). This difference is most likely due to

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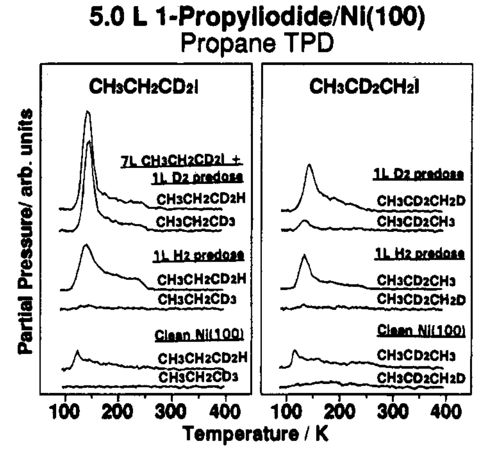

Figure 6. Propane ($C_3H_6D_2$ and $C_3H_5D_3$) TPD spectra from 5.0 L $CH_3CH_2CD_2I$ (left) and 5.0 L $CH_3CD_2CH_2I$ (right) dosed on clean (bottom) and hydrogen (center) and deuterium (top) predosed Ni(100) surfaces. All the exposures were carried out at 90 K.

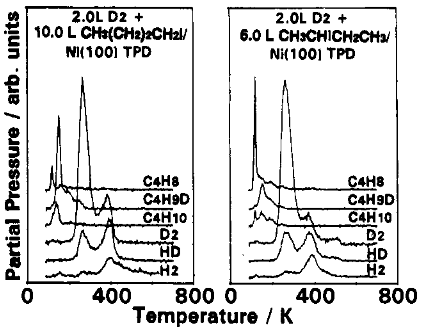

Figure 7. H_2, HD, D_2, C_4H_{10}, C_4H_9D, and C_4H_8 TPD spectra from Ni(100) surfaces first dosed with 2.0 L deuterium and then with either 10.0 L 1-iodobutane (left) or 6.0 L 2-iodobutane (right).

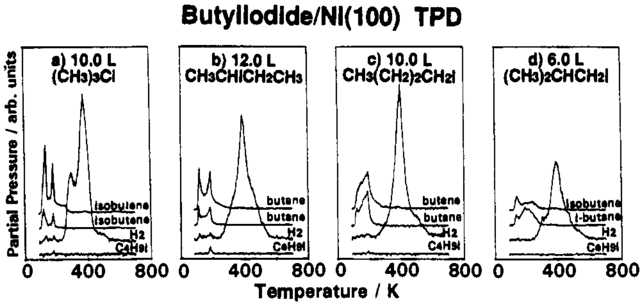

Figure 8. Iodobutane, hydrogen, butane, and butene TPD spectra from Ni(100) surfaces dosed with 10.0 L 2-iodo-2-methylpropane (a), 12.0 L 2-iodobutane (b), 10.0 L 1-iodobutane (c), and 6.0 L of 1-iodo-2-methylpropane (d) at 90 K.

a kinetic isotope effect, which amounts to a difference of about 1−2 kcal/mol between the activation of C−H and C−D bonds.[6]

The formation of alkanes in these systems is believed to take place via the reductive elimination of the surface alkyl groups with coadsorbed hydrogen atoms. When alkyl iodides are dosed on clean nickel surfaces, the hydrogen atoms needed for this reaction originate from both adsorption of background gases and the β-H elimination step responsible for the formation of the olefin. Alternatively, this hydrogen can be provided by predosing the surface with hydrogen. Again, isotope labeling experiments were used to corroborate this mechanism. For instance, Figure 6 shows $CH_3CH_2CD_2H$ as the only hydrogenation product from adsorbed $CH_3CH_2CD_2I$; no significant amount of $CH_3CH_2CD_3$ desorbs in this case. The yield of $CH_3CH_2CD_2H$ increases in the presence of coadsorbed hydrogen because of the recombination of the hydrogen atoms with $CH_3CH_2CD_2$ species. Likewise, both $CH_3CH_2CD_3$ and $CH_3CH_2CD_2H$ are detected in the presence of coadsorbed deuterium, now because the $CH_3CH_2CD_2$ species can recombine with either predosed deuterium or background hydrogen. For $CH_3CD_2CH_2I$, the TPD spectra show both $CH_3CD_2CH_3$ and $CH_3CD_2CH_2D$ production even on the clean surface; the latter comes from the recombination of $CH_3CD_2CH_2$ species with the D atom generated by the β-deuteride elimination step. The respective yields for $CH_3CD_2CH_3$ and $CH_3CD_2CH_2D$ increase in the presence of coadsorbed H or D respectively, as expected. The preferential formation of $CH_3CD_2CH_3$ in the presence of normal surface hydrogen in particular argues against a concerted disproportionation step between two adjacent alkyl groups to produce the alkane and the olefin simultaneously.

Additional TPD experiments were also performed with surfaces dosed sequentially with deuterium and either 1- or 2-iodobutane. The results, summarized in Figure 7, indicate that only H_2, HD, D_2, C_4H_{10}, C_4H_9D, and C_4H_8 desorb in either case. The production of C_4H_9D is explained by the direct incorporation of a deuterium atom into the C_4H_9 species, while C_4H_{10} formation involves hydrogen from the background. The main difference between the two cases reported in this figure is that 1-iodobutane hydrogenates preferentially to butane (the butene-to-butane ratio is only 0.1), while both butane and butene are produced in approximately equal amounts from 2-iodobutane. In both cases, the increase in yield and the decrease in peak temperature in the alkane TPD peak induced by hydrogen coadsorption suggests that alkane formation from alkyl groups on the clean surface is limited by the availability of hydrogen atoms. This is most likely the reason why, in the absence of coadsorbed hydrogen, the traces for alkane and alkene formation are quite similar.

As already mentioned above, the general features of the thermal chemistry of 1-iodo-2-methylpropane are reproduced by other alkyl iodides. To illustrate this point, Figure 8 shows temperature-programmed desorption spectra obtained from saturation coverages of all possible isomers of butyl iodide chemisorbed on Ni(100) single crystal surfaces. Again, only hydrogen and the two expected hydrocarbons are produced in each case: both 1- and 2-iodobutane decompose to butene and butane, and both 1- and 2-iodo-2-methylpropane form isobutene and isobutane. Hydrogen desorbs mainly about 390 K in all cases, but the H_2 TPD peak shape is different for each compound, and additional features are seen at lower temperatures in some of the spectra. More interestingly are the reactivity trends highlighted by the data for the desorption of the hydrocarbons. Both an alkene and an alkane are always produced in these systems, but the alkene-to-alkane yield ratio varies significantly from case to case. Looking at the high temperature peaks in the TPD traces (the ones associated with surface reactions) in the case of 2-iodo-2-methylpropane [$(CH_3)_3CI$], the yield for isobutene is about 4.4 times that for isobutane. Both products desorbs in two sharp peaks about 130 and 180 K, and the only significant difference between the traces of the two hydrocarbons is that there is an additional small shoulder in the olefin TPD spectrum around 220 K (Figure 8a). The thermal activation of 2-iodobutane ($CH_3CHICH_2CH_3$) leads to the desorption of both butene and *n*-butane, again in two peaks (now at about 115 and 185 K), but the butene-to-butane ratio in this case is only 1.4, about 3 times smaller than that for 2-iodo-2-methylpropane (Figure 8b). The TPD spectra for 1-iodobutane [$CH_3(CH_2)_3I$] are similar to the two described above, the main differences being in the intensity of the low-temperature peaks for butene and butane desorption (which are not as big as those from the 2-iodobutane), in the shape of the high temperature peaks (which are broad and centered around

Table 1

	$(CH_3)_3CI$	$CH_3CHICH_2CH_3$	$CH_3(CH_2)_2CH_2I$	$(CH_3)_2CHCH_2I$
no. of β-H	9	5	2	1
total yield/ML[a]				
alkene	0.32	0.28	0.23	0.07
alkane	0.07	0.20	0.27	0.14
alkene/alkane ratio	4.4	1.4	0.84	0.58
alkene peak T/K				
low T	130	115	125	135
high T	180	185	190	210
peak shape (high T)	sharper	→		broader
E_a/kcal/mol[b]	10.4	10.7	11.0	12.2
$A/10^{12}$ s^{-1} [c]	48	20	9	0.5

[a] Monolayers, as number of molecules per Ni surface atom. [b] Using Redhead's equation and a preexponential factor of 10^{13} s^{-1}. [c] Preexponential factor, assuming E_a = 11.0 kcal/mol.

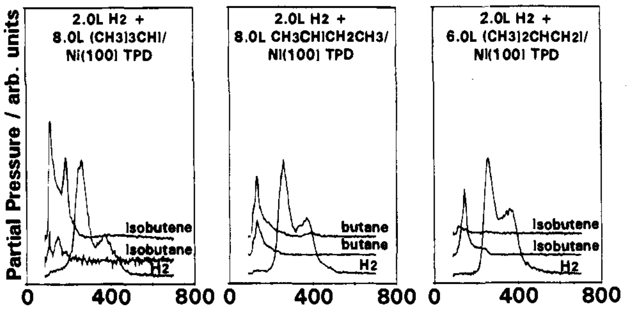

Figure 9. H_2, butane, and butene TPD spectra from Ni(100) surfaces dosed with 8.0 L 2-iodo-2-methylpropane (a), 8.0 L 2-iodobutane (b), and 6.0 L 1-iodo-2-methylpropane (c), after predosing with 2.0 L normal hydrogen.

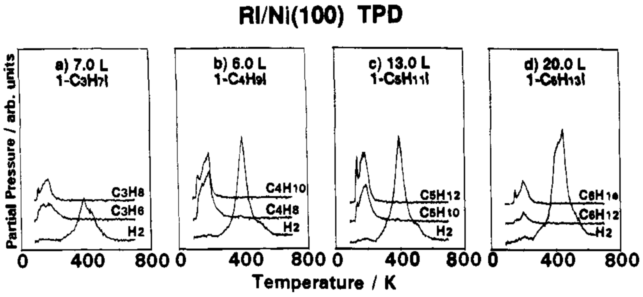

Figure 10. H_2, alkene, and alkane TPD spectra from Ni(100) surfaces dosed with 7.0 L 1-iodopropane (a), 6.0 L 1-iodobutane (b), 13.0 L 1-iodopentane (c), and 20.0 L 1-iodohexane (d) at 90 K.

190 K), and in the butene-to-butane ratio (which in the high-temperature regime is only 0.84) (Figure 8c). Finally, the alkene (isobutene)-to-alkane (isobutane) ratio obtained from 1-iodo-2-methylpropane [$(CH_3)_2CHCH_2I$] is 0.58, but the high-temperature features in this case are quite different for the alkane and the alkene, even though both peak above 200 K, a higher temperature than in all the other cases (Figure 8d). The results from all of these experiments are summarized in Table 1.

The effect of coadsorbed hydrogen on the reactivity of alkyl groups was explored as well. As an example, the TPD traces obtained from surfaces where 2.0 L H_2 was coadsorbed with 2-iodo-2-methylpropane, 2-iodobutane, and 1-iodo-2-methylpropane are shown in Figure 9. In all cases, hydrogen desorption was observed in two stages, about 260 and 360 K. The high-temperature peak corresponds to hydrogen desorption from recombination of the H atoms generated from alkyl decomposition, the same as before. The low-temperature, however, seems to be the results of a repulsive interaction between some of the coadsorbed hydrogen and the C_4 iodides, as suggested by the results from recent isotope labeling experiments.[7,8] With respect to the formation of hydrocarbons, the yields for both butene and butane production remain practically unchanged with the addition of coadsorbed hydrogen for the case of 2-iodo-2-methylpropane. The β-hydride elimination to isobutene still dominates the overall chemistry (Figure 9a), with a isobutene-to-isobutane ratio of about 4.3, only slightly lower than that obtained without hydrogen coadsorption. Nevertheless, the high-temperature isobutene desorption peak does shift slightly, to 185 K. More significant changes were observed in the other two cases. The coadsorption of 2.0 L H_2 with 2-iodobutane, for instance, causes the butene and butane TPD peaks to collapse into one feature around 130 K and causes a change in the butene-to-butane ratio to a value of 0.6, about two times lower than without hydrogen coadsorption (Figure 9b). This effect is even more noticeable for the 1-iodo-2-methylpropane case, where the coadsorbed hydrogen makes the production of isobutane dominate the overall chemistry (Figure 9c). In terms of absolute yields, they do not change significantly in the case of 2-iodo-2-methylpropane with or without hydrogen coadsorption, but the alkene production decreases by about 50% for 2-iodobutane and 1-iodo-2-methylpropane, while alkane formation increases by 20% and 40%, respectively.

Finally, the effect of chain length on the relative yields from β-H and reductive elimination reactions was explored. The TPD spectra obtained for 1-iodopropane, 1-iodobutane, 1-iodopentane, and 1-iodohexane are summarized in Figure 10. As in the case of the other iodoalkanes, only hydrogen, an alkene, and an alkane desorb in each case. The alkene-to-alkane yield ratio was found to change with varying chain length; the longer the alkyl chain, the smaller the ratio. For example, values of about 1.1 and 0.47 were obtained for 1-iodopropane and 1-iodohexane, respectively. The key results from these experiments are summarized in Table 2.

4. Discussion

The results presented here provide some insight into the details of the thermal chemistry of alkyl iodides on Ni(100) surfaces. In particular, trends in activities and selectivities for the different reactions available to these compounds were identified as a function of both chain branching and chain length. First of all, the I 3d XPS data presented in Figure 3 indicate that below 100 K the alkyl iodide chemisorption is molecular: the binding energies observed in our experiments are typical of nondissociated alkyl iodides at those temperatures. This conclusion is consistent both with previously reported results for CH_3I, C_2H_5I, and C_3H_7I on the same surface[4,5,6] and with other work function and vibrational studies on Ag, Cu, and Pt surfaces.[19-21] Our data are also consistent with the notion that these molecules

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Table 2

	$CH_3CH_2CH_2I$	$CH_3(CH_2)_2CH_2I$	$CH_3(CH_2)_3CH_2I$	$CH_3(CH_2)_4CH_2I$
alkene/alkane ratio	1.1	0.84	0.76	0.47
alkene peak T/K				
low T	110	125	130	150
high T	170	190	190	200
high T peak				
Ea/kcal/mol[a]	9.8	11.0	11.0	11.6
$A/10^{12}\ s^{-1}$ [b]	310	9	9	2

[a] Using Redhead's equation and a preexponential factor of $10^{13}\ s^{-1}$. [b] Preexponential factor, assuming $E_a = 11.0$ kcal/mol.

interact with the surface through the iodine atom[19-21] and with the idea that the overall chemisorption geometry changes with coverage. The D_2 TPD titration experiments presented here (Figure 1) suggest that at low coverages the alkyl chains tend to maximize their interaction with the metal by lying down flat on the surface. The XPS results obtained for alkyl iodides of different sizes, on the other hand, indicate that the saturation coverage is approximately the same regardless of the chain length of the alkyl (Figure 2). These two facts lead to the conclusion that at high coverages the molecules are well packed on the surface and, therefore, have their main axis oriented perpendicular to the surface plane. This change in adsorption geometry with coverage has been reported previously for other system as well.[10,11,22-24]

Next, on the basis of the shifts in I 3d binding energies observed with increasing annealing temperatures (Figure 3), it can be concluded that alkyl iodides start to decompose on the Ni(100) surface around 120 K via the cleavage of the C−I bond. Several other studies have shown that these C−I bonds are indeed quite labile, requiring only about 2−4 kcal/mol for their activation regardless of the particular alkyl compound being considered.[4-6,25] The main products from the C−I bond breaking step are iodine atoms and alkyl surface groups.[4-6]

The reactivity of the resulting alkyl species on the surface depends on the initial adsorption geometry of the alkyl iodide. At low coverages they dehydrogenate readily to surface carbon and hydrogen atoms, which recombine and desorb around 300 K; the decomposition mechanism in this regime is unknown at the present time. At saturation coverages, however, the thermal activation of any alkyl groups with hydrogen at the β position yields significant amounts of alkenes and alkanes. The desorption of each of these hydrocarbons occurs in two different temperature regimes, in a low-temperature peak only seen at high coverages and believed to involve the formation of alkyl free radicals,[12] and above 150 K, in a feature that originates from reactions that occur on the surface. It is quite possible that alkenes are also produced at low coverages, but that they dehydrogenate immediately after being formed. Indeed, TPD experiments with both propene and butene have shown that olefin molecular desorption starts only at coverages around half-saturation. Nevertheless, this hypothesis still needs to be tested.

The results from isotopic labeling experiments with both ethyl and propyl iodides have shown that the formation of alkenes in the high-temperature regime occurs via a β-hydride elimination step.[5,6] This type of reaction involves the transfer of a hydrogen from the second (or β) carbon atom of the alkyl chain to the metal surface. The TPD data for the propyl iodides shown in Figure 5 proves that the β-hydride elimination is highly preferred over either α- or γ-hydride elimination steps.[5,6] Alkane formation, on the other hand, occurs mostly via the reductive elimination of alkyl groups with surface hydrogen atoms, which are either produced by the β-elimination step, or adsorbed from background or predosed gases (Figures 6, 7, and 9). A small amount of alkane can also be generated by the hydrogenation of the alkene produced from the β-hydride elimination reaction.[8] However, no products from either hydrogenolysis or C−C coupling reactions were ever detected during the thermal decomposition of alkyl iodides on this nickel surface.

The particular characteristics of the desorption peaks for the alkanes and alkenes in the high-temperature regime (the one associated with the surface reactions) were shown to depend on the nature of the alkyl group. For instance, the isobutene produced by the decomposition of 1- and 2-iodo-2-methylpropanes desorbs at about 210 and 180 K, respectively (Figure 8). The fact that the same alkene is seen at different temperatures in TPD experiments from different alkyl iodides is a good indication that the limiting step is the surface reaction responsible for the formation of the olefin (the β-hydride elimination step), and not the desorption of the product. The same can be said for the *n*-butene produced by 1- and 2-iodobutane activation and for the butanes produced in all cases. Moreover, the alkane TPD traces almost always parallel the alkene TPD curves, indicating that the hydrogenation of the alkyl groups on the clean surface is limited by the β-hydride elimination step (the reaction that provides the required extra hydrogen atom). The presence of coadsorbed hydrogen on the surface sometimes shifts the temperature for the formation of the alkanes to lower values, an indication of a decrease in the apparent activation energy and an increase in overall rate that can be explained by a change in the rate limiting step.[7,26] We have shown in the past that alkyl reductive elimination steps do have activation energy barriers several kcal/mol lower than those of β-hydride elimination reactions.[8]

The yield ratio between alkene and alkane production from alkyl iodides depends on both the length and the degree of branching of the initial alkyl chain (Tables 1 and 2). For instance, the more substituted the β-carbon atom, the lower the alkene-to-alkane ratio is. Also, β-hydride elimination occurs at higher temperatures in molecules with fewer β-hydrogens: 2-iodo-2-methyl-propane, which has the least substituted β-carbon atom and the most number of β-hydrogens (nine), produces isobutene at about 180 K, while the butenes from 2-iodobutane, 1-iodobutane, and 1-iodo-2-methylpropane desorb at 185, 190, and 210 K, respectively (Figure 8). The TPD peaks becomes sharper in the compounds with more β-hydrogens as well. It is interesting to speculate on the reasons for these changes. One obvious explanation for all of this is that the observed behavior is due to either entropic or steric effects. Assuming a constant activation energy of 11.0 kcal/mol for all reactions, the preexponential factor, calculated by Redhead's equation,[27] changes from a value of 48×10^{12} to 20×10^{12}, 9×10^{12}, and

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0.5×10^{12} s^{-1} when going from 2-iodo-2-methylpropane to 2-iodobutane, 1-iodobutane and 1-iodo-2-methylpropane, respectively. This sequence follows quite closely the changes in the number of β-hydrogens, suggesting that the differences in rate are due to a pure statistical factor. However, this argument cannot explain all the results reported here. For instance, the large alkene-to-alkane ratio for 2-iodo-2-methylpropane is due not only to an increase in the rate of the β-hydride elimination step, but also to the hindrance of the reductive elimination of the isobutyl group with hydrogen because of steric effects. This is why the yield for alkane formation does not increase significantly in this case in the presence of coadsorbed hydrogen. Activation of 1-iodobutane, 2-iodobutane, and 1-iodo-2-methylpropane, on the other hand, do result in lower alkene-to-alkane ratios when hydrogen is coadsorbed on the surface, mainly because the absolute yield for the reductive elimination increases (Figures 7 and 9).

It should be also noted that a higher degree of substitution at the β-position not only decreases the alkene yield, but also increases the peak temperature for the decomposition of the alkyl groups on the surface (Table 1). This suggests that the rate of the elimination reaction may also depend on energetic factors. In fact, the length of the alkyl chain was shown to play a role in determining this reactivity, even when they all have the same number of β-hydrogens. An increase in the length of the alkyl carbon chain leads to both a decrease of the alkene-to-alkane ratio and an increase in desorption temperature: the ratio goes from 1.1 for 1-iodopropane to about 0.47 for 1-iodohexane, and the desorption temperature changes from about 170 to 200 K (Table 2). The possible energetic contribution to this effect can be illustrated by calculating activation energies using Redhead's approach and assuming a constant preexponential factor of 10^{13} s^{-1}.[27] Values for the activation energy of the formation and subsequent desorption of both alkenes and alkanes in those calculations increase from 10.4 to 10.7, 11.0, and 12.2 kcal/mol in going from 2-iodo-2-methylpropane to 2-iodobutane, 1-iodobutane, and 1-iodo-2-methylpropane, respectively, and from 9.8 to 11.0, 11.0, and 11.6 kcal/mol in going from 1-iodopropane to 1-iodobutane, 1-iodopentane, and 1-iodohexane, respectively. It is possible that in the latter sequence the dominant factor is the van der Waals interaction between chains in adjacent changes, which increases by a couple of kcal/mol with each additional methylene group.

Energetic factors alone cannot justify the experimental observations either. Recent experiments with fluorinated alkyl groups have indicated that the β-hydride elimination step proceeds via the extraction of a negative ion and the formation of a transition state where the β-carbon develops a partial positive charge.[28] On the basis of this mechanism, it would be expected that the activation of a 2-methyl propyl moiety would be easier than that of a *tert*-butyl group, where all β-hydrogens are primary, and for the reactivity of *n*-butyl to also be higher than that of *sec*-butyl moieties. The fact that the experimental results follow the opposite trends indicate that energetic considerations are not enough to explain the differences in reactivity in these systems. The inclusion of both entropic and energetic contributions in the determination of reaction rates is required to obtain a complete picture of the behavior reported here for the chemistry of alkyl groups on transition metal surfaces. Lastly, it is interesting to note that a trend opposite to that seen here for nickel has been reported for aluminum surfaces.[29,30]

Finally, the decomposition of *neo*-pentyl iodide was shown to produce *neo*-pentyl groups on the surface, in a similar fashion as other alkyl iodides. Since those species lack β-hydrogens, however, they are much more stable than any of the other alkyl groups studied here. The only alkene produced from the thermal decomposition of *neo*-pentyl moieties is isobutene, which desorbs at around 390 K, about 200 K higher temperature than the others.[31] The activation energy of the limiting step responsible for the isobutene desorption was estimated to be of the order of 22 ± 2 kcal/mol, a value too high to be associated with steps related to either olefin desorption or hydrogen abstraction, and more in line with the breaking of C−C bonds. Additional isotope labeling experiments have also proven that the bond which breaks in that case is that between the α- and β-carbons. The results from those experiments will be discussed in more detail in a separate publication.[32]

5. Conclusions

In this report we have shown that the thermal decomposition of saturation coverages of alkyl iodides on Ni(100) surfaces yields mostly alkenes and alkanes. The alkene-to-alkane product ratio from this process was shown to depend on chain substitutions as well as on chain length. It was found that alkene formation is greatly favored over alkane production on alkyl iodides with a highly substituted α-carbon atom (containing the most number of β-hydrogen atoms). Alkyl hydrogenation, on the other hand, was proven to dominate for alkyl iodides with a small number of β-hydrogen atoms (compounds such as 1-iodo-2-methyl-propane). Increasing the chain length has the effect of decreasing the alkene-to-alkane ratio as well. These trends were discussed in terms of both energetics and entropic changes in the limiting β-hydride elimination step. Coadsorption of hydrogen on the surface was found to increase the yield for alkane formation, but this effect was shown to be significant only for the less branched alkyls.

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