The Thermal Chemistry of Neopentyl Iodide on Ni(100) Surfaces: Selectivity between α-C−H and γ-C−H and between C−H and C−C Bond-Scission Steps in Chemisorbed Neopentyl Moieties

Francisco Zaera* and Sariwan Tjandra

Contribution from the Department of Chemistry, University of California, Riverside, California 92521

Received August 12, 1996[⊗]

Abstract: The thermal chemistry of neopentyl iodide on Ni(100) single-crystal surfaces was characterized under vacuum by using temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). The first decomposition step, which takes place around 150 K, is the scission of the C−I bond, the same as in other chemisorbed alkyl halides. Owing to the absence of *β* hydrogens, however, no easy decomposition pathway is available for the resulting neopentyl surface species. Neopentane is produced via neopentyl reductive elimination with surface hydrogen, and desorbs in two stages around 140 and 180 K. The yield for this pathway is approximately 45% of the initial neopentyl iodide at saturation (which is approximately 0.2 ML) on the clean nickel, but reaches a value close to 100% if enough hydrogen (or deuterium) is predosed on the surface. The other major carbon-containing product from neopentyl iodide activation is isobutene, which desorbs around 400 K. Isotope labeling experiments demonstrated that the C−C bond that breaks in that reaction is the one between the α and *β* carbons, and highlighted the fact that the kinetics of the overall reaction displays strong isotope effects upon deuterium substitution at either the α or *γ* positions. In addition, the hydrogen TPD traces indicated that one of the two hydrogens from the α carbon of the neopentyl group is removed at low temperatures (below 300 K), suggesting that the precursor to isobutene formation is a neopentylidene intermediate.

1. Introduction

Previous studies have shown that alkyl iodides are ideal precursors for the preparation of alkyl groups cleanly on metal surfaces.[1−4] Indeed, the initial thermal activation of alkyl iodides on most transition metals leads to the scission of their C−I bond and to the generation of alkyl fragments and iodine atoms on the surface. The resulting alkyl fragments can then be used to study the reactions involved in hydrocarbon conversion processes such as Fisher−Tropsch synthesis and alkane activation.[5,6] Our recent studies on Ni(100) have shown that small alkyl fragments undergo both hydrogenation and dehydrogenation reactions to form alkanes and alkenes, respectively;[7−10] the alkene is produced via 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.[11−13]

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 neopentyl iodide on Ni(100) surfaces. Since this is one of the simplest molecules with no hydrogens at the *β* position, it is ideal for testing the selectivity between α- and *γ*-hydride elimination steps. It was found that removal of an α-hydrogen occurs selectively below 300 K and yields neopentylidene moieties on the surface, and that the subsequent activation of that intermediate produces gas-phase isobutene. The C−C bond scission involved in the latter reaction occurs exclusively at the α−*β* position, and displays strong kinetic isotope effects upon substitution of hydrogens for deuteriums at either the α or *γ* positions. The results reported here are discussed in terms of a possible mechanism for the overall neopentyl conversion.

2. Experimental Details

All experiments were performed in an ultrahigh vacuum (UHV) apparatus described in detail elsewhere[7,14] The chamber is evacuated by a turbomolecular pump to a base pressure below 1×10^{-10} Torr, and is equipped with instrumentation for temperature-programmed desorption (TPD), X-ray photoelectron (XPS), secondary-ion mass (SIMS), Auger electron (AES), and ion scattering (ISS) spectroscopies. TPD spectra were obtained by using a heating rate of about 10 K/s, and by recording the mass-spectrometric signals of up to 15 different masses simultaneously in a single experiment with an interfaced computer. The TPD signal intensities are reported in absolute desorption rates, in monolayer/s, after calibrating the original signals from the mass spectrometer as follows: (1) the raw data, which represent desorption fluxes, were first converted into values proportional to partial pressures by correcting for the differences in desorption temperature (by multiplying them by the square root of the temperature); (2) the signal for hydrogen was then calibrated by comparison with the TPD from a hydrogen-saturated Ni(100), which was estimated to be about 1 ML (defined as one adsorbate per nickel surface atom) of

---

[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1996.

(1) Zaera, F. *Acc. Chem. Res.* **1992**, *25*, 260.
(2) Zaera, F. *J. Mol. Catal.* **1994**, *86*, 221.
(3) Zaera, F. *Chem. Rev.* **1995**, *95*, 2651.
(4) Zhou, X.-L.; Zhu, X.-L.; White, J. M. *Acc. Chem. Res.* **1990**, *23*, 327.
(5) Vannice, M. A. *Catal. Rev.-Sci. Eng.* **1976**, *14*, 153.
(6) Hubert, A. *Catalysis in C₁ Chemistry*, Keim, W., Eds.; (Reidel Publishing Co.: Dordretcht, 1983.
(7) Tjandra, S.; Zaera, F. *Langmuir* **1992**, *8*, 2090.
(8) Tjandra, S.; Zaera, F. *Surf. Sci.* **1993**, *289*, 255.
(9) Tjandra, S.; Zaera, F. *Langmuir* **1994**, *10*, 2640.
(10) Tjandra, S.; Zaera, F. *J. Am. Chem. Soc.* **1995**, *117*, 9749.
(11) Tjandra, S.; Zaera, F. *J. Catal.* **1993**, *144*, 361.
(12) Tjandra, S.; Zaera, F. *J. Catal.* **1994**, *147*, 598.
(13) Tjandra, S.; Zaera, F. *Surf. Sci.* **1995**, *322*, 140.
(14) Zaera, F. *Surf. Sci.* **1989**, *219*, 453.

atomic hydrogen;[15,16] and (3) the other signals were referenced to that of hydrogen by measuring relative sensitivities when leaking equal pressures of the gases of interest (hydrogen, methane, isobutene, neopentane, and neopentyl iodide). 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 (fwhm). The energy scale was calibrated by using binding energy values for the Pt $4f_{7/2}$ and Cu $2p_{3/2}$ signals of 70.9 and 932.4 eV, respectively.[14]

The nickel single crystal was cut and polished in the (100) orientation by 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 side of the crystal. Cleaning of the crystal was done by oxygen treatment and argon ion sputtering cycles followed by annealing to about 1000 K until no impurities were detected by either AES or XPS. The nonisotopically labeled neopentyl iodide ($C_5H_{11}I$) was purchased from Aldrich, and was subjected to several freeze−pump−thaw cycles before introduction into the vacuum chamber. The neopentyl-α-d_2 iodide was synthesized by reduction of trimethyl acetyl chloride (Aldrich, 99%) with lithium aluminum deuteride (Aldrich, 98% D)[17] and subsequent reaction of the resulting neopentyl-α-d_2 alcohol with phosphorus triiodide (Aldrich, 99%) in carbon disulfide (Aldrich, 99.9%).[18] The neopentyl-γ-d_9 iodide was made via the reaction of neopentyl-γ-d_9 alcohol with triphenyl phosphite (Aldrich, 97%) and methyl iodide.[19] The alcohol-d_9 was in turn prepared from acetone-d_6 (Aldrich, 99.5%), via pinacol-d_{12} and the corresponding pinacolone;[20] the oxidation of that pinacolone to pivalic-d_9 acid was accomplished by using a solution of sodium hydroxide and bromine (Aldrich, 99.99%),[21] and the reduction of the pivalic acid to the alcohol by adding lithium aluminum hydride (Aldrich, 95%) to the solution.[17] The purity of all compounds was checked initially by NMR and periodically in situ in our vacuum chamber by mass spectrometry. Surface exposures are reported in langmuirs (1 L $= 1 \times 10^{-6}$ Torr·s), not corrected for differences in ion gauge sensitivities.

3. Results

The thermal chemistry of neopentyl iodide on Ni(100) was first studied by temperature-programmed desorption (TPD). The identification of the desorbing products was achieved by following the evolution of a large number of molecular fragments during several TPD experiments, including the 2−4, 16−20, 28, 39−44, 55−60, 70−73, 112, 127, 142, 198, and 200 amu's. Only four major products were seen to desorb from this system, namely, hydrogen, isobutene, neopentane, and neopentyl iodide. A small amount (less than 0.05 ML) of methane was occasionally detected around 200 K, but this was not reproducible, and most likely originated from either impurities or surface defects.

The TPD traces for hydrogen (2 amu, panel a), isobutene (56 amu after deconvolution of the low-temperature contribution from neopentane, panel b), neopentane (57 amu, panel c), and neopentyl iodide (198 amu, panel d) are shown as a function of initial neopentyl iodide exposure in Figure 1. Hydrogen, which is the only desorbing product at low coverages (after exposures below 2.0 L), appears as one main peak around 360 K and a high temperature tail about 450 K. The temperature of the main feature is approximately the same as for hydrogen desorption from H_2 adsorbed on clean Ni(100),[15] suggesting that the neopentyl iodide molecules decompose completely at low temperatures. Increasing the initial coverage of neopentyl iodide on the surface leads to a shift of the hydrogen desorption to higher temperatures, and to a split into three features (Figure 1a); after a 6.0 L dose the three peaks are centered at approximately 330, 405, and 490 K, and correspond to roughly 20, 70, and 10% of the total area, respectively.

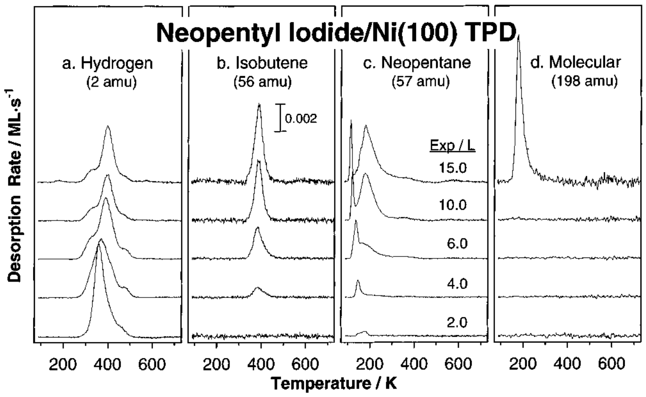


Figure 1. Hydrogen (2 amu, a), isobutene (56 amu, b), neopentane (57 amu, c), and neopentyl iodide (198 amu, d) temperature-programmed desorption (TPD) spectra from neopentyl iodide adsorbed on Ni(100) at 90 K as a function of initial exposure. The scale bar provided in panel b for the desorption rates applies to all the panels in this figure. A heating rate of about 10 K/s was used in these experiments.

Isobutene desorption starts after initial exposures of 4.0 L or more, and the TPD peak, initially centered around 395 K, grows and shifts slightly (to approximately 400 K) with increasing coverage (Figure 1b). A small amount of neopentane desorption does occur at low coverages, as shown by the broad double peak with maxima around 150 and 180 K seen in the trace for the 2.0 L exposure (Figure 1c), and that signal grows, sharpens, and shifts to lower temperatures (140 K) by 4.0 L. Even higher neopentyl iodide exposures result in the appearance of three features in the neopentane TPD, one sharp one that goes from 135 to 110 K as the dose is increased from 6.0 to 15.0 L, a broader peak centered around 175 K that grows later in intensity, and a third small feature around 380 K that appears as a bump in the high-temperature tail of the second peak. The low temperature peak may perhaps be associated either with the ejection of neopentyl radicals from neopentyl iodide decomposition[22,23] or with a direct reaction between neopentyl iodide and chemisorbed hydrogen,[11] but the other features are most likely associated with the reductive elimination of neopentyl surface moieties with hydrogen (see Discussion). Finally, molecular desorption is seen only after monolayer saturation, after an exposure slightly below 10.0 L, and appears as a single sharp peak about 178 K.

The product yields calculated from the areas of the TPD traces shown in Figure 1 are displayed as a function of initial neopentyl iodide dose in Figure 2. The yield for molecular hydrogen desorption is highest at low coverages, but never amounts to more than 0.25 ML (where 1 ML is again defined as one adsorbate moiety per nickel surface atom). Mass balance arguments indicate that this desorption corresponds to the total decomposition of approximately 0.04 ML of neopentyl iodide for the 2.0 and 4.0 L cases, and to only 0.024 and 0.008 ML for the 6.0 and 10.0 L exposures, respectively. The nonzero value (about 0.04 ML) shown for hydrogen after a 0.0 L neopentyl iodide dose was obtained by following the exact same protocol as in the other measurements (except for the neopentyl

---

(15) Christmann, K.; Schober, O.; Ertl, G.; Neumann, M. *J. Chem. Phys.* **1974**, *60*, 4528.

(16) Zhu, X.-Y.; White, J. M. *J. Phys. Chem.* **1988**, *92*, 3970.

(17) Nystrom, R. F.; Brown, W. G. *J. Am. Chem. Soc.* **1947**, *69*, 2548.

(18) Hudson, H. R. *J. Chem. Soc.* **1968**, 664.

(19) Rydon, H. N. *Org. Syn.* **1971**, *51*, 44.

(20) Adams, R.; Adams, E. W. *Org. Syn.* **1941**, *1*, 459.

(21) Puntambeker, S. V.; Zoellner, E. A. *Org. Syn.* **1941**, *1*, 524.

(22) Lin, J.-L.; Bent, B. E. *J. Am. Chem. Soc.* **1993**, *115*, 2849.

(23) Zaera, F.; Tjandra, S. *J. Phys. Chem.* **1994**, *98*, 3044.

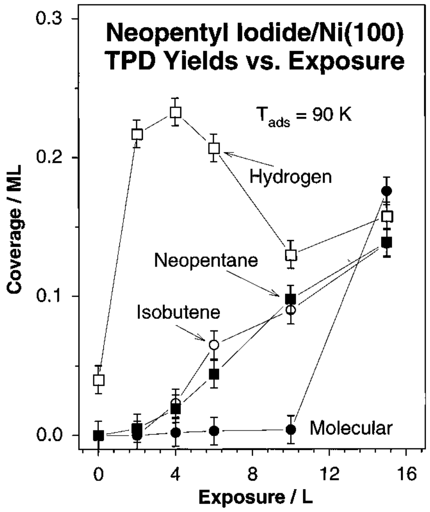


Figure 2. Desorption yields from TPD experiments with neopentyl iodide adsorbed on Ni(100) surfaces as a function of initial exposure.

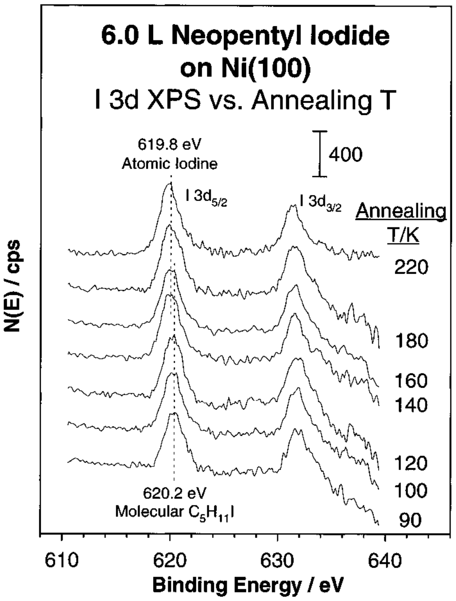


Figure 3. I 3d X-ray photoelectron spectra (XPS) from 6.0 L of neopentyl iodide adsorbed on Ni(100) as a function of annealing temperature. The shift in the I $3d_{5/2}$ and $3d_{3/2}$ peaks around 150 K is associated with the dissociation of the adsorbed iodide molecules into neopentyl surface species and atomic iodine.

dosing), and represents an upper limit for the amount of adsorption from the background that takes place in these experiments (see also the isotope labeling experiments discussed later). Neopentane and isobutene desorption start above about 1.0 and 3.0 L, respectively, and their yields are approximately equal and grow approximately linearly with exposure afterwards, reaching values of up to about 45% of the total neopentyl iodide conversion each at high coverages.

The TPD data presented above were complemented with both iodine and carbon XPS studies. Figure 3 shows the I 3d XPS traces obtained after adsorbing 6.0 L of neopentyl iodide on Ni(100) at 90 K and then annealing to the indicated temperatures. Two peaks are initially seen around 620.2 and 631.7 eV, corresponding to the $3d_{5/2}$ and $3d_{3/2}$ photoelectron signals from iodine in neopentyl iodide, respectively.[8,14] Those features do not change in shape or area as the surface is heated, but do shift by about 0.4 eV toward lower binding energies around 150 K, a transition associated with the scission of the C−I bond.[8,14] Additional spectra were taken after dosing 15.0 L of the iodide at 90 K and annealing to 180 K to desorb any molecular neopentyl iodide in order to calibrate the surface coverages. It was estimated that saturation is reached after exposures of about 7.0 L, and corresponds to approximately 0.20 ML of iodine,[10] in reasonable agreement with the results obtained by TPD.

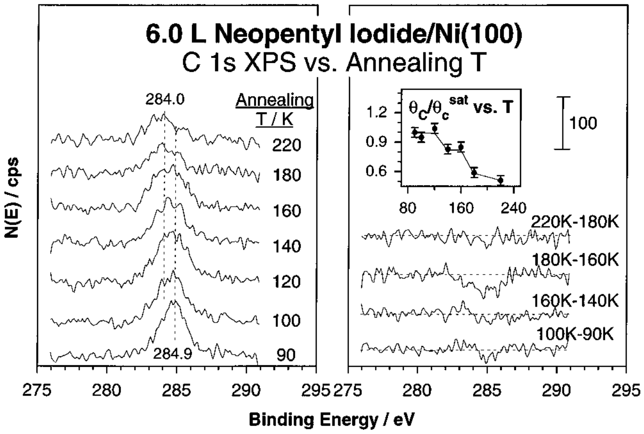


Figure 4. Left: C 1s XPS from 6.0 L of neopentyl iodide adsorbed on Ni(100) as a function of annealing temperature. Right: Difference spectra calculated from the raw data shown in the left panel to highlight the changes that occur on the surface upon heating. Inset: Calculated carbon surface coverages as a function of annealing temperature. The peak shifts seen below 160 K are associated with the conversion of neopentyl iodide to neopentyl surface species, while the reduction in carbon surface concentration reflects the depletion of the surface species due to the desorption of neopentane.

The corresponding C 1s XPS annealing data are shown in Figure 4. The 6.0 L of molecular neopentyl iodide initially adsorbed at 90 K yields a peak around 284.9 eV and a possible small shoulder in the low binding energy side. Annealing of that sample at different increasing temperatures induces several changes, as better illustrated by the difference spectra displayed in the right panel of Figure 4. Heating to temperatures as low as 100 K results in a shift in intensity from the main original peak to the shoulder around 283.2 eV. No significant changes are then observed up to 120 K, but at 140 K the peak intensity is reduced by about 15%, and further intensity shifting from the high to the low binding energy features occurs at 160 K. Between 160 and 180 K there is a significant loss in peak intensity, about another 25% of the initial signal (see inset in the right panel), and by 220 K only one small peak below 284.0 eV is left in the spectra. The intensity loss in going from 90 to 220 K is most likely associated with the desorption of neopentane, and amounts to a total of about 50% of the initial signal, in good agreement with the TPD data (which gave a value of 45 ± 5%).

The mechanism for neopentane formation was probed further by TPD experiments with coadsorbed deuterium. The left panel of Figure 5 displays typical TPD raw data for the case of a Ni(100) surface sequentially dosed with 2.0 L of D_2 and 6.0 L of normal (nondeuterated) neopentyl iodide at 90 K. Two major species desorb in this case, namely, hydrogen (of all isotopic compositions) and neopentane. Hydrogen desorption is identified by the traces for 2, 3, and 4 amu, which correspond to H_2, HD, and D_2, respectively; the preadsorbed deuterium desorbs mainly around 265 K, although high temperature shoulders can be seen at 320 and 340 in the D_2 and HD traces, respectively, while normal hydrogen from neopentyl iodide decomposition evolves predominantly about 385 K. With respect to the neopentanes, their production is manifested by the large peaks at 145 and 235 K in the remaining traces (41 and 56−59 amu). In order to analyze these data further, it is necessary to point

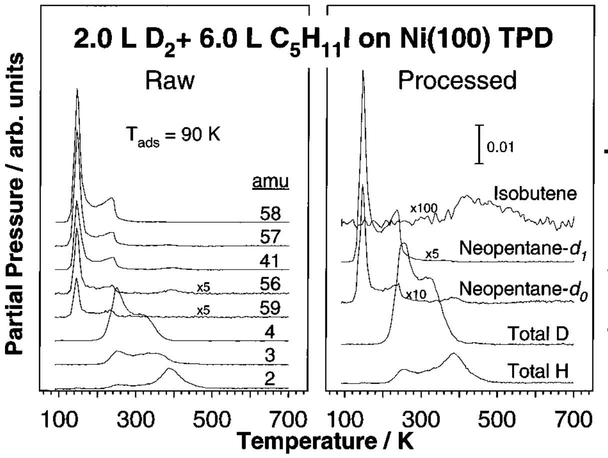


Figure 5. Left: 2, 3, 4, 59, 56, 41, 57, and 58 amu TPD raw traces from 6.0 L of neopentyl iodide adsorbed on a Ni(100) surface predosed with 2.0 L of deuterium. Right: Corresponding total H, total D, neopentane-d_0, neopentane-d_1 and isobutene calculated TPD data. The formation of isobutene is inhibited almost completely by the coadsorbed deuterium, and no neopentane isotopomers other than d_0 and d_1 are produced in this system either.

out that the cracking pattern of neopentane in the mass spectrometer shows almost no signal for the molecular peak; the main contribution to the mass spectra of those species comes from the formation of a *tert*-butyl cation in the ionizing region.[24] Therefore, while the spectrum of normal neopentane displays one prominent peak at 57 amu (and a small one at 58 amu 0.044 times the size of that at 57 amu due to the normal abundance of ^{13}C in the hydrocarbon molecules), that of neopentane-d_1 has two peaks at 57 and 58 amu with 1:3 relative intensities (if isotope effects are neglected), and neopentane-d_2 has peaks at 57, 58, and 59 amu with relative intensities going from 1:0:3 for pure 2,2-dimethylpropane-1,1-d_2 to 0:2:2 for pure 2,2-dimethylpropane-1,3-d_2. With this in mind, we can proceed with the interpretation of the TPD in Figure 5. First of all, the low-temperature peaks seen in the traces for 56 and 59 amu can be accounted for by the cracking and ^{13}C contributions from neopentane-d_0 and neopentane-d_1, so no neopentane-d_2 forms in this system. This means that no H-D scrambling occurs on the surface, and that only normal and monodeuterated neopentanes are detected, from which the production of the d_1 isotopomer accounts for about 80% of the total. Also, results from other isotope-labeling experiments (not shown here) indicate that the d_0 production is due to incorporation of normal hydrogen from background adsorption into neopentyl surface groups. It is interesting to point to two more observations related to neopentane desorption: (1) the relative high-to-low temperature yield ratio (between the 235 and 145 K contributions to the TPD traces) is higher for neopentane-d_1 than for neopentane-d_0 (that is, more monodeuterated neopentane is produced in relative terms at high temperatures); and (2) a small amount of neopentane-d_0 (but no neopentane-d_1) is produced around 385 K, as in the case of normal neopentyl iodide on clean Ni(100). Finally, a small amount of isobutene is also produced even in the presence of surface deuterium, note the peaks about 400 K in the traces for 41 and 56 amu, but this (normal) isobutene amounts to less than 2% of the total initial neopentyl iodide adsorbed on the surface, and is only observed after alkyl iodide exposures above 5.0 L. The processed data are shown in the right panel of Figure 5.

The evolution of the TPD traces as the initial neopentyl iodide exposure is increased in the experiments with 2.0 L of predosed D_2 was explored next (data not shown). After exposures above 1.0 L of the iodide, the total yields for both hydrogen and deuterium remain approximately constant (at about 0.12 and 0.30 ML, respectively), but the peak shapes change significantly upon increasing hydrocarbon coverage, with the bulk of the signal intensity shifting to the low-temperature features. Since this effect is more pronounced in the case of deuterium, which is preadsorbed on the surface and therefore does not originate from hydrocarbon decomposition, it must be related to changes in adsorption energy with coadsorption, as reported previously for other systems.[11] In terms of the formation of neopentane, the main effect induced by the coadsorbed deuterium is to increase its yield at the expense of neopentyl decomposition. This is particularly noticeable for the low-temperature peak, which is most likely associated with reactions involving the direct conversion of the neopentyl iodide to neopentane[23,25] In addition, increasing coverages of neopentyl iodide on the deuterium-covered nickel surface lead to a broadening of the neopentane TPD peaks toward higher temperatures, from below 200 K after a 0.5 L dose to around 235 K after 6.0 L. The relative production of neopentane-d_1 over neopentane-d_0 is more important in this latter feature (as compared to that at the low temperature), either because of kinetic isotope effects or because of a difference in reaction mechanisms (reactions with neopentyl iodide vs neopentyl surface species). Interestingly enough, the small desorption peak around 380 K is only seen in the neopentane-d_0 traces, most likely because the hydrogen atom required for neopentyl hydrogenation at those high temperatures originates from the decomposition of other surface moieties, not from hydrogen (deuterium) preadsorption; note that this reaction occurs at the onset of the formation of isobutene.

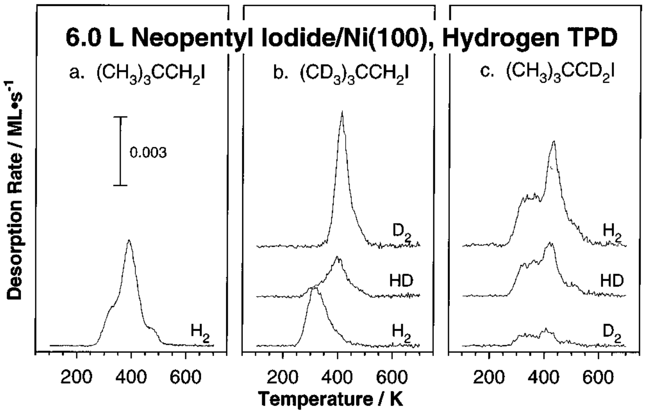


Figure 6. Hydrogen (H_2, HD, and D_2) TPD spectra from 6.0 L of normal ($(CH_3)_3CCH_2I$, a), γ-d_9 ($(CD_3)_3CCH_2I$, b), and α-d_2 ($(CH_3)_3CCD_2I$, c) neopentyl iodides adsorbed on clean Ni(100) at 90 K. The low-temperature dehydrogenation of neopentyl surface groups involves only one hydrogen atom from the α position, as indicated by the 330 K peak seen for deuterium in panel c (and the absence of any D_2 signal below 400 K in panel b), and presumably produces neopentylidene moieties on the nickel substrate.

The results from TPD experiments with partially-deuterated neopentyl iodides are shown in Figures 6, 7, and 9; the desorption traces for hydrogen (in all its isotopomers, H_2, HD and D_2) are shown in Figure 6, and those for neopentane and isobutene in Figures 7 and 9, respectively. Three different isotopically substituted neopentyl iodides were used here, namely, the normal, nondeuterated compound ($(CH_3)_3CCH_2I$), and the α-d_2 ($(CH_3)_3CCD_2I$) and γ-d_9 ($(CD_3)_3CCH_2I$) deuterium-substituted isotopomers. Regarding the desorption of hydrogen, the most interesting observation from these experiments comes from comparing the low-temperature (330 K) peaks in the traces

---

(24) *Registry of Mass Spectral Data*; Stenhagen, E., Abrahamson, S., McLafferty, F., Eds.; Wiley-Interscience: New York, 1974.

(25) Tjandra, S.; Zaera, F. *J. Am. Chem. Soc.* **1992**, *114*, 10645.

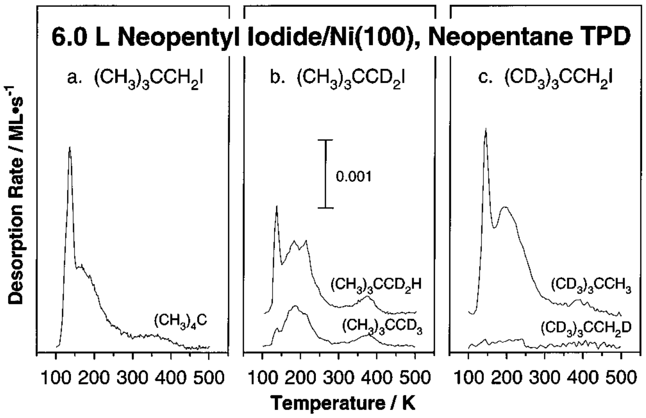


Figure 7. Neopentane TPD spectra from 6.0 L of normal ($(CH_3)_3CCH_2I$, a), α-d_2 ($(CH_3)_3CCD_2I$, b), and γ-d_9 ($(CD_3)_3CCH_2I$, c) neopentyl iodides adsorbed on clean Ni(100) at 90 K. The significant production of neopentane-d_3 from neopentyl-α-d_2 iodide seen in panel b implies the incorporation of deuterium atoms into the neopentyl surface groups at temperatures as low as 150 K, and therefore points to an early α-H (α-D) elimination step from those moieties.

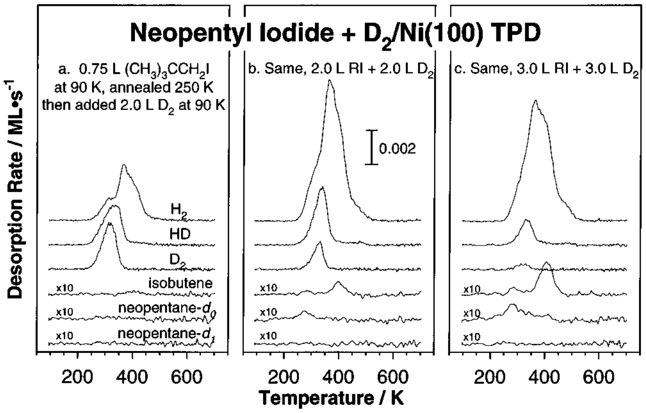


Figure 8. H_2, HD, D_2, isobutene, neopentane-d_0, and neopentane-d_1 TPD spectra from Ni(100) surfaces first dosed with neopentyl iodide at 90 K, then annealed at 250 K to activate the C−I bond, and finally exposed to deuterium at 90 K. Different doses were used in these experiments: 0.75 L of neopentyl iodide and 2.0 L of deuterium (a), 2.0 and 2.0 L of the iodide and D_2, respectively (b), and 3.0 and 3.0 L (c). The absence of any significant neopentane desorption in all cases points to the irreversible nature of the first α-H elimination step from neopentyl surface species.

for the γ- and α-deuterated compounds shown in the two right panels of Figure 6; while most of the hydrogen produced at that temperature comes out as H_2 in the first case, it contains a significant amount of deuterium in the second. In fact, about half of the total deuterium that originates from neopentyl-α-d_2 decomposition does desorb below 390 K, indicating that an α-hydrogen (deuterium) elimination step from those surface moieties takes place at temperatures much below those needed for either isobutene production or total dehydrogenation.

The fact that at least one α-H elimination step occurs at low temperatures, probably below 150 K, is corroborated by the neopentane TPD data displayed in Figure 7. The formation of neopentane from neopentyl iodide requires the incorporation of an additional hydrogen atom, which originates either from surface decomposition of some of the adsorbed hydrocarbons or from adsorption from the background. The fact that some normal H is added to the neopentyl moieties in all three cases studied here implies that the latter source of hydrogen can never be ruled out, but the absence of any significant production of neopentane-d_{10} from neopentyl-γ-d_9 iodide indicates that no γ-hydrogens are involved in the hydrogenation process; the scission of any of the γ-C−H bonds must require temperatures much higher than those leading to neopentane desorption. In contrast, a significant amount of neopentane-d_3 is produced in the case of neopentyl-α-d_2 iodide, by incorporation of a deuterium atom which can only come from α-deuterium elimination from surface neopentyl groups. That deuterium is the one that desorbs in the low-temperature hydrogen TPD reported above.

The first dehydrogenation step mentioned in the last paragraph appears to be irreversible. This hypothesis was tested by performing experiments where a clean Ni(100) surface was first dosed with neopentyl iodide at 90 K, then annealed at 250 K, and finally exposed to D_2 again at 90 K. The idea here was to try to induce the deuteration of the surface species that forms after thermal activation of the neopentyl iodide past the temperature of the first dehydrogenation step. The results from three of those TPD runs are shown in Figure 8. Both the neopentyl iodide and the deuterium exposures used were varied in an attempt to balance two opposite trends, namely, the difficulty in hydrogenating neopentyl groups at low coverages, and the blocking of sites for deuterium adsorption after high neopentyl iodide exposures. Some deuterium adsorption does take place even after a 3.0 L dose of neopentyl iodide on the surface, as indicated by the observable signal in the D_2 and (more noticeable) HD TPD traces in the right panel of Figure 8, but that deuterium uptake is much lower than when the adsorption order is reversed (compare the corresponding traces in Figures 5 and 8), so lower alkyl iodide exposures were used as well (Figure 8, left panels). The main observation from these experiments is that, once heated to 250 K, the neopentyl groups dehydrogenate irreversibly on the surface, because no deuterated neopentane can be produced afterwards; either 2.0 or 3.0 L doses of neopentyl iodide are sufficient to induce significant hydrogenation if the adsorption of both the alkyl iodide and the deuterium is done at low temperatures (data not shown). Also noteworthy is the fact that some normal (nondeuterated) neopentane is indeed made around 280 K, most likely by hydrogenation of the few neopentyl moieties that may remain undissociated at that temperature; when the annealing temperature before deuterium dosing was increased to 280 K, no neopentane formation was observed at all (results not shown). Finally, a small amount of isobutene desorbs around 400 K, especially in the 3.0 L neopentyl case, another indication of the irreversible dehydrogenation that leads to surface decomposition.

Additional information on the mechanism for isobutene formation can be extracted from the isobutene TPD data from the experiments with the isotopically-labeled compounds shown in Figure 9. Notice in particular the high selectivity for normal and perdeuterio isobutene formation from the neopentyl-α-d_2 and -γ-d_9 iodides, respectively. This result points to the specificity of the carbon−carbon bond-breaking step at the α−β position, and therefore rules out the β-methyl elimination mechanism proposed in an earlier report,[26] because in that case d_2 and d_6 olefins (respectively) should have been produced instead (see Discussion). There is also a clear shift in the temperature maxima of the isobutene TPD peak with deuterium substitution, an effect that is more noticeable in the case of the neopentyl-α-d_2 case. In order to minimize the problems associated with comparing data from different TPD experiments, the TPD for both the normal and d_2-substituted compounds were repeated approximately a dozen times in different occasions over a period of more than a year; the isobutene TPD peaks were found to reach maxima at 387 ± 8 and 415 ± 15 K (95%

---

[26] Zaera, F.; Tjandra, S. *J. Am. Chem. Soc.* **1993**, *115*, 5851.

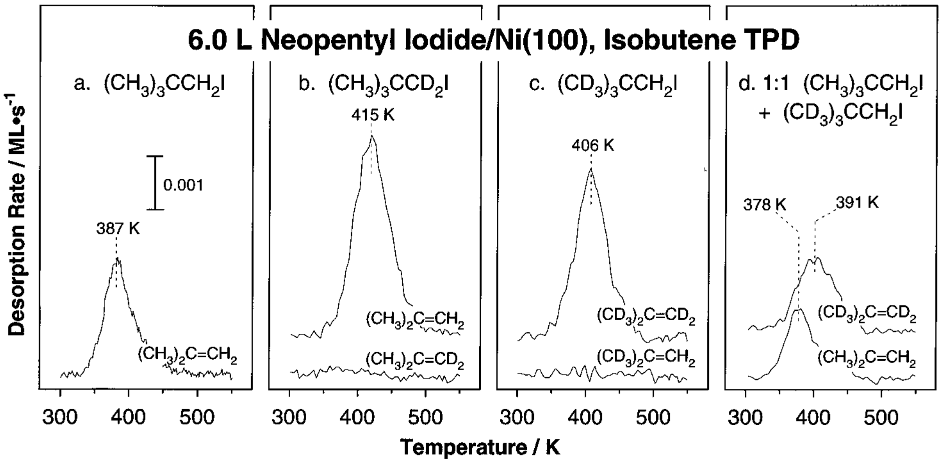


Figure 9. Isobutane TPD spectra from 6.0 L of normal ($(CH_3)_3CCH_2I$, a), α-d_2 ($(CH_3)_3CCD_2I$, b), γ-d_9 ($(CD_3)_3CCH_2I$, c), and a 1:1 mixture of normal and γ-d_9 neopentyl iodides adsorbed on clean Ni(100) at 90 K. Normal and perdeuterio isobutenes are produced exclusively from neopentyl-α-d_2 and -γ-d_9 iodides, respectively, indicating that the only C−C bond that breaks in this reaction is that between the α and β positions. Significant kinetic isotope effects upon deuterium substitutions at either α or γ positions are also evidenced by the shifts in the corresponding TPD peaks.

confidence), respectively. This large difference is clearly outside the statistical fluctuations of the experiments.

A kinetic isotope effect was also detected between the neopentyl-d_0 (normal) and neopentyl-γ-d_9 iodides, but of a smaller magnitude than in the case of the d_2 compound; here the isobutene peak maximum shifts only from 387 to 406 K. Fortunately, the products in this case have different isotopic composition (C_4H_8 vs C_4D_8), and can therefore be separated easily by mass spectroscopic methods. In order to eliminate any errors from running two separate experiments, a single TPD determination was made for the kinetics of formation of both isobutene products by using a 1:1 $(CH_3)_3CCH_2I + (CD_3)_3CCH_2I$ mixture, the result of which is shown in the last panel of Figure 9. Only two isotopomers of the olefin were detected, the normal and perdeuterio isobutenes, and those peaked at significantly different temperatures, 378 and 391 K, respectively. This clearly demonstrates that deuteration at the γ position also induces a change in the kinetics for the production of isobutene.

Finally, the possibility of an early C−C bond-breaking step, at temperatures below those where isobutene desorption is observed, was also probed. The TPD from 3.0 L of isobutene adsorbed on clean Ni(100) (not shown) indicate a high degree of decomposition, as seen by a large signal for H_2 desorption between 250 and about 500 K; only about 5% of the original olefin desorbs molecularly, in a sharp peak at 138 K and a broader and smaller feature around 230 K. Preadsorption of methyl iodide on the surface does not significantly alter the chemistry of adsorbed isobutene, but the TPD in that case displays an increase in molecular isobutene desorption (still at 138 and 230 K) and the formation of a small amount of methane about 220 K (from hydrogenation of methyl groups[11]). One last experiment was designed to better simulate the surface that may result from neopentyl thermal activation in which the preadsorbed methyl iodide was annealed to 160 K before adsorption of the isobutene in order to break the C−I bond.[7,27] The results in this case were quite similar to those where the adsorption was all carried out at low temperature, only that a little less methane was produced. No high-temperature isobutene desorption was detected in any of these cases, and extensive dehydrogenation was always observed below 400 K (over 95% of the hydrogen produced desorbs below that temperature).

4. Discussion

As already mentioned in the Introduction, alkyl halides (the iodides in particular) have been used extensively in recent years as precursors for the preparation of alkyl surface groups on metal surfaces.[1] The weak C−I bond in those compounds can be easily activated, and breaks below 200 K on Ni(100) and other surfaces.[10,14,28−30] The same low-temperature C−I bond scission was seen here for the case of neopentyl iodide on Ni(100): the XPS spectra shown in Figure 3 display the shifts in I 3d binding energies (from 620.2 to 619.8 eV when heating above 150 K in the case of the I $3d_{5/2}$ peak) typically associated with the detachment of the iodine atom from the molecule into the surface,[14] and the data presented in Figure 4 indicate that the C 1s XPS signal changes in that temperature range as well.

Activation of the C−I bond in adsorbed neopentyl iodide most likely leads to the formation of neopentyl groups on the surface. Spectroscopic evidence has been provided in the past for the isolation of other alkyl groups on similar systems,[1,9,29,31−34] and, although no direct evidence for the formation of chemisorbed neopentyl groups was acquired in our case, some of the TPD results reported above support the hypothesis that such groups do form on the Ni(100) surface as well. In particular, alkyl groups have been shown to undergo a facile reductive elimination step with coadsorbed hydrogen (or deuterium) to yield the corresponding alkane,[11−13,35,36] and that was observed here: almost half of the initial neopentyl iodide molecules adsorbed on clean Ni(100) produce neopentane at high coverages, and almost quantitative conversion via that reaction is obtained on hydrogen (or deuterium) predosed surfaces. Furthermore, the reaction of neopentyl iodide with surface deuterium produces almost exclusively neopentane-d_1, strongly suggesting that it is a surface neopentyl group that is being reduced in this process. It should be noticed that some of the neopentane detected in the TPD experiments appears at quite low temperatures, below

---

(27) Tjandra, S.; Zaera, F. *Langmuir* **1993**, *9*, 880.

(28) Tjandra, S.; Zaera, F. *J. Vac. Sci. Technol.* **1992**, *A10*, 404.

(29) Lin, J.-L.; Bent, B. E.; *J. Phys. Chem.* **1992**, *96*, 8529.

(30) Zaera, F.; Hoffmann, H. *J. Phys. Chem.* **1991**, *95*, 6297.

(31) Jenks, C. J.; Bent, B. E.; Bernstein, N.; Zaera, F. *J. Am. Chem. Soc.* **1993**, *115*, 308.

(32) Zaera, F.; Bernstein, N. *J. Am. Chem. Soc.* **1994**, *116*, 4881.

(33) Zhou, X.-L.; White, J. M. *Surf. Sci.* **1988**, *194*, 438.

(34) Lloyd, K. G.; Roop, B.; Campion, A.; White, J. M. *Surf. Sci.* **1989**, *214*, 227.

(35) Zaera, F. *J. Phys. Chem.* **1990**, *94*, 8350.

(36) Zaera, F. *Surf. Sci.* **1992**, *262*, 335.

140 K, and could therefore originate from a reaction involving the original iodide.[23] Nevertheless, the peak about 180 K, which accounts for more than half of the total neopentane, is clearly associated with neopentyl surface species.

The interesting and unique observation from the studies reported in this paper relates to the subsequent thermal decomposition of the neopentyl surface moieties on the Ni(100) surface. Most alkyl groups dehydrogenate readily via a β-hydride elimination step to yield the corresponding olefin,[1,3] but since neopentyl groups have no hydrogens at the β position, they can not follow such a pathway. The only hydrocarbon product other than neopentane detected in the TPD experiments with neopentyl iodide on Ni(100) is isobutene, which desorbs around 400 K.[26] The rest of this discussion will deal with the mechanism that leads to the formation of that olefin.

The first point that needs to be made is that neopentyl surface species dehydrogenate at relatively low temperatures, perhaps below 150 K, via an α-hydride elimination step. Both the regioselectivity and the stoichiometry of this step were proven by the hydrogen TPD data from partially-labeled neopentyl iodides shown in Figure 6; the traces from experiments with $(CD_3)_3CCH_2I$ show practically no deuterium desorption below 380 K, indicating that no γ-C−H (C−D) bonds break before that temperature, and the intensity of the deuterium desorption signal from $(CH_3)_3CCD_2I$ decomposition is split approximately evenly between the two peaks below and above 400 K, which means that one of the two deuterium atoms in that molecule is released early on during the heating of the sample. The point at which this α-H elimination takes place can not be established accurately with the TPD data from this study, but several pieces of information do point to a low temperature for this process. In particular, the TPD results from $(CH_3)_3CCD_2I$ displayed in Figure 7 indicate a high yield for the formation of neopentane-d_3; that molecule is produced via the reductive elimination of the neopentyl-α-d_2 groups with surface deuterium, and the only possible source for the latter is the α-H (α-D) elimination step mentioned above. Since neopentane production via hydrogenation of surface neopentyl groups starts around 150 K, that must be an upper limit for the temperature of the dehydrogenation reaction.

α-Hydride elimination from neopentyl moieties presumably produces surface neopentylidene ($(CH_3)_3CCH{=}Ni_x$) species. It appears as if such intermediates, once formed on Ni(100), cannot be easily hydrogenated back to either neopentyl or neopentane, and are stable up to close to 400 K. All attempts to either hydrogenate or deuterate this species by post-dosing deuterium after neopentyl iodide activation failed (see Results). In addition, no other reactions were seen to take place on these surfaces before the production of isobutene. That no more dehydrogenation steps occur below 400 K is proven by the fact that the only hydrogen desorption seen below that temperature in the TPD is that associated with the α-H elimination reaction; all other hydrogen atoms desorb above 400 K, implying that their detection is limited by the surface reaction(s) that produces them. With respect to C−C bond-breaking steps, they must also take place at high temperatures, because (1) carbon−carbon bond-scission steps usually display high activation energies, above 15 kcal/mol;[3,37−39] (2) if *tert*-butyl groups were to be made on the surface, they would undergo β-hydride elimination and produce isobutene below 180 K;[10] and (3) if isobutene were to be produced at any point above 140 K during the TPD experiments, it would either immediately desorb molecularly or dehydrogenate to surface carbon and hydrogen (as indicated by the TPD experiments with coadsorbed methyl iodide and isobutene mentioned in the Results). All this leads to the conclusion that the production of isobutene seen in the TPD data from neopentyl iodide on Ni(100) occurs via a concerted rearrangement on neopentylidene moieties.

A few additional points can be made concerning the conversion of neopentylidene to isobutene based on the results presented here. First of all, the isobutene TPD experiments with α- and γ-labeled compounds shown in Figure 9 illustrate the high regioselectivity of the C−C bond-breaking step: normal (d_0) and perdeuterio (d_9) isobutenes are produced exclusively from neopentyl-α-d_2 and neopentyl-γ-d_9 iodides, respectively, indicating that the bond that breaks is that between the α and β carbons. In addition, deuterium substitutions at either the α or γ positions induce noticeable normal kinetic isotope effects. The magnitude of these rate changes upon deuteration can be estimated by comparing reaction rates at a fixed temperature in the TPD data, and comes out to be on the order of factors of 5−7 and 2−3 for the α-d_2 and γ-d_9 cases, respectively. Alternatively, the activation energy for isobutene formation, estimated by using either Redhead's equation[40] or a leading edge analysis,[41] is about 18 ± 2 kcal/mol for normal neopentyl iodide (the preexponential factor being approximately 10^{10} s^{-1}), and approximately 1.5 and 1.0 kcal/mol higher for the d_2 and d_9 compounds, respectively. These changes in energy barrier with deuterium substitution are typical of primary isotope effects and can not be easily accounted by changes in the mass of the leaving group (which would lead to a maximum change in rate of about 5% for the γ-substituted system). In conclusion, the data presented here strongly suggest that the formation of isobutene from neopentylidene on Ni(100) surfaces involves a concerted step where all C−C and α- and γ-C−H bond scissions occur simultaneously (or at least are all involved in the rate-limiting step). Alternatively, it is possible (although less likely) for neopentylidene to undergo two slow and competitive α- and γ-H elimination steps in parallel. The resulting neopentylidyne and α,α,γ-tricoordinated metallacycle intermediates would then have to produce isobutene via a series of fast decomposition reactions.

Even though it is difficult to envision how the concerted conversion of neopentylidene to isobutene may take place on this Ni(100) surface (a proposal for this is shown schematically in Scheme 1), several of the mechanisms seen in other systems can be ruled out here. First of all, the hypothesis of a β-methyl elimination pathway postulated in our earlier studies,[26] which was based on analogies with organometallic systems,[42] can now be discarded because of the results shown in Figure 9, which unequivocally prove the high selectivity for the cleavage of the C−C bond at the α−β position (no loss of methyl groups is involved in this step). The most common reaction followed by alkyl groups with no β hydrogens on late transition metals is, in fact, a γ-hydride elimination,[43] either involving a metal-hydride intermediate,[44] or via a direct abstraction by electrophilic attack of another metal−carbon bond in a four-center transition state;[45] the resulting metallacyclobutane can then in principle undergo a ring opening to the observed olefin (and a surface

---

(37) Goodman, D. W. *Surf. Sci.* **1982**, *123*, L679.

(38) Zaera, F.; Somorjai, G. A. *J. Phys. Chem.* **1985**, *89*, 3211.

(39) Rodriguez, J. A.; Goodman, D. W. *Surf. Sci. Rep.* **1991**, *14*, 1.

(40) Redhead, P. A. *Vacuum* **1962**, *12*, 203.

(41) Habenschaden, E.; Küppers, J. *Surf. Sci.* **1984**, *138*, L147.

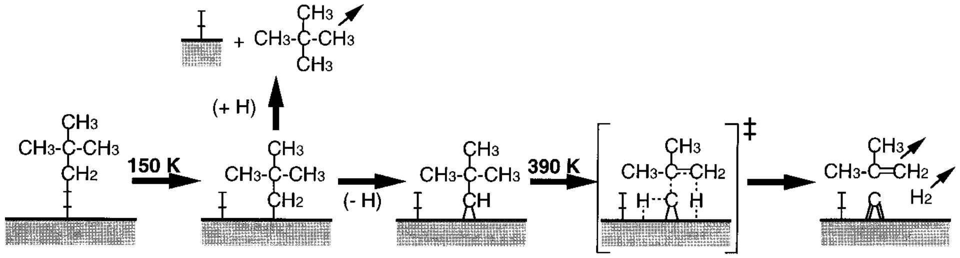
(42) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51.

(43) Collman, J. P.; Hegedus, L. S.; Norton, J. R. Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(44) Foley, P.; DiCosimo, R. Whitesides, G. M. *J. Am. Chem. Soc.* **1980**, *102*, 6713.

(45) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425.

Scheme 1



carbene), as in metathesis processes.[46,47] Both the formation of a 3,3-dimethyl nickelacyclobutane from the corresponding dineopentyl−metal complex and its subsequent decomposition to isobutene have in fact been reported recently.[48] There are nevertheless several reasons why this mechanism is not consistent with our observations for the neopentyl/Ni(100) system: (1) no γ-hydrogens are activated below 400 K, which means that if a metallacycle were to form on the nickel surface, it would have to be produced at that high temperature, and would have to decompose immediately afterwards; (2) because an early α-H elimination is seen in the hydrogen TPD of deuterium-labeled compounds, an alkylidene, not alkyl, species is believed to be the starting moiety in the high-temperature conversion of neopentyl to isobutene; (3) if isobutene were to be produced via the ring opening of a 3,3-dimethyl nickelacyclobutane intermediate, the probabilities for α-β and β-γ C−C bond scissions would be approximately equal, an expectation inconsistent with the high selectivity seen here toward the activation of the C_α−C_β bond; and (4) a γ-hydride elimination rate-limiting step can not account for the large kinetic isotope effect upon deuterium substitution at the α position of the neopentyl moiety reported above.

A related mechanism to the one discussed in the previous paragraph involves an initial direct carbene extrusion from the original neopentyl moiety[43,49] and a subsequent β-hydride elimination from the resulting *tert*-butyl surface species to isobutene. The preferential C−C bond cleavage at the α position via this type of mechanism was proven for the case of a nickelacyclohexane complex by using deuterium labeling.[50] This idea, however, can be discarded in our case as well, because (1) again, the starting reactant on the nickel surface is neopentylidene, not neopentyl; and (2) since the β-hydride elimination that must follow the extrusion is fast, this mechanism would not induce any kinetic isotope effects upon substitution at the γ position.

The alternative initial α-hydride elimination reported here has indeed been seen in organometallic compounds, especially of early transition metals.[51−53] However, the resulting alkylidenes most often dehydrogenate further to alkylidynes,[54] and those are quite stable, even though they occasionally dimerize to produce alkynes.[55,56] In some clusters alkylidyne dehydrogenation to μ-vinylidene has been observed instead,[57] but such a reaction does not lead to the α-β C−C bond scission reported here, and is not even available on neopentyl groups (which do not have β hydrogens). Two more reactions are available to coordinated carbenes, namely, direct dimerization[58] and 1,2-shift[59] to the corresponding alkenes, but both those steps are more common with Fischer-type carbenes, and do not explain the isobutene formation seen here either.

Given the importance of alkyls as intermediates in the catalytic conversion of alkanes (in reactions such as hydrogenation−dehydrogenation, re-forming, and partial and total oxidation), extensive work has been done on those systems as well.[60−62] The catalytic H−D exchange of neopentane on nickel films has been shown to be limited mostly to one methyl group, and to yield neopentane-d_1 and -d_3 as the major products.[63] A mechanism was proposed for this reaction where the initial surface neopentyl intermediate that forms after neopentane activation follows one of two competing pathways, a reductive elimination with surface deuterium to neopentane-d_1, or a fast interconversion with an α,α-diadsorbed species (neopentylidene) followed by a slower hydrogenation to neopentane-d_3. These ideas are entirely consistent with the results of our work.

The catalytic H-D exchange on neopentane is usually accompanied by slower hydrogenolysis and isomerization processes. Three basic mechanisms have been proposed to explain these reactions: (1) a direct isomerization via an α,α,γ-tricoordinated bridged species;[64] (2) the intermediate isomerization of that tricoordinated metallacycle to a monocoordinated cyclopentyl species;[65] and (3) a methyl transfer via a cyclopentane-like intermediate, the same as in the bond-shift mechanism in carbonium ions.[66,67] It is important to point out, however, that these ideas have been put forward mainly to explain isomerization reactions (from neopentane to 2-methylbutane in this case), and such processes are seen almost exclusively on platinum-based catalysts. No isomerization is observed in the case of nickel, only the production of isobutane (as well as smaller amounts of methane, ethane and propane).[63] The bottom line is that none of the mechanisms enumerated above is supported by the evidence obtained from our experiments. Finally, it is interesting to note that on Pt(111) surfaces

---

(46) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491.

(47) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring Opening Polymerization of Cycloolefins*; Wiley: New York, 1986.

(48) Miyashita, A.; Ohyoshi, M.; Shitara, H.; Nohira, H. *J. Organometal. Chem.* **1988**, *338*, 103.

(49) Stenstrøm, Y.; Klauck, G.; Koziol, A.; Palenik, G. J.; Jones, W. M. *Organometallics* **1986**, *5*, 2155.

(50) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 7418.

(51) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc, Dalton Trans.* **1979**, 1121.

(52) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

(53) Cross, R. J. in *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Vol. 2; pp 559−624.

(54) Churchill, M. R.; Wasserman, H. J.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 1710.

(55) McDermott, G. A.; Mayr, A. *J. Am. Chem. Soc.* **1987**, *109*, 580.

(56) Kim, H. P.; Angelici, R. J. *Adv. Organometal. Chem.* **1987**, *27*, 51.

(57) Rashidi, M.; Puddephatt, R. J. *Organometallics* **1988**, *7*, 1636.

(58) Merrifield, J. H.; Lin, G.-Y.; Kiel, W. A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5811.

(59) Fischer, E. O.; Schubert, U.; Fischer, H. *Pure Appl. Chem.* **1878**, *50*, 587.

(60) Bond, G. C. *Catalysis by Metals*; Academic Press: London, 1962.

(61) Kemball, C. *Adv. Catal. Relat. Subj.* **1959**, *11*, 223.

(62) Zaera, F.; Somorjai, G. A. In *Hydrogen Effects in Catalysis: Fundamentals and Practical Applications*; Paál, Z.; Menon, P. G., Eds.; Marcel Dekker: New York, 1988; pp 425−447.

(63) Kemball, C.; Kempling, J. C. *Proc. R. Soc. London A* **1972**, *329*, 391.

(64) Anderson, J. R.; Avery, N. R.; *J. Catal.* **1966**, *5*, 446.

(65) Garin, F.; Gault, F. G. *J. Am. Chem. Soc.* **1975**, *97*, 4466.

(66) McKervey, M. A.; Rooney, J. J.; Samman, N. G. *J. Catal.* **1973**, *30*, 330.

(67) Karpinski, Z.; Guczi, L. *J. Chem. Soc., Chem. Commun.* **1977**, 563.

it has been shown that α- and γ-hydride elimination steps display similar rates,[68] in contrast with the case of Ni(100), where selective α-hydride elimination is seen instead.

5. Conclusions

The chemistry of neopentyl iodide on Ni(100) surfaces has been characterized by temperature-programmed desorption and X-ray photoelectron spectroscopies, and is summarized in Scheme 1. The same as in the case of most other alkyl iodides, the first reaction that takes place on this system is the scission of the C−I bond, presumably to produce neopentyl surface groups. At high coverages about half of these neopentyl moieties undergo an early reductive elimination step with surface hydrogen (or deuterium) to neopentane, which is detected in the gas phase below or around 180 K. The other half remains on the surface, and no other hydrocarbon products desorb from this surface until reaching temperatures around 400 K, at which point isobutene is formed. Isotope labeling experiments indicate that the chemisorbed neopentyl intermediates dehydrogenate below or about 150 K to neopentylidene, and that this neopentylidene is the one that converts to the olefin. The experimental data also point to the selective scission of the α-β C−C bond, and to primary kinetic isotope effects in the neopentylidene conversion to isobutene with deuterium substitution at either the α or γ positions. All this suggests a concerted step involving the $C_\alpha-C_\beta$ bond and two hydrogen atoms, and rules out most of the decomposition pathways reported in the literature for alkyl and carbene ligands in organometallic compounds.

Acknowledgment. Financial support for this research was provided by a grant from the National Science Foundation (CHE-9530191).

JA9628056

---

[68] Janssens, T. V. W.; Jin, G.; Zaera, F. *J. Am. Chem. Soc.*, submitted for publication.