Evidence for a New Reaction in Organic/Metal Systems: Elimination of Methyl Groups from Alkyl Species Chemisorbed on Nickel Surfaces

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Recent surface science studies suggest that the electronic interaction between discrete molecules and solid substrates is in most cases localized[1] and that there should be a close correlation between surface and organometallic systems.[2] At the same time, it has also become clear that there are some differences between those two types of systems. In this communication we report an example involving neopentyl groups that nicely illustrates this point where decomposition via a β-methyl elimination is preferred over other more common alternatives such as α- and γ-hydride elimination, coupling, and radical formation.[3-5]

The experiments reported here were conducted in an ultrahigh vacuum (UHV) stainless steel bell jar evacuated to base pressures below 1×10^{-10} Torr and equipped with instrumentation for thermal programmed desorption (TPD) and X-ray photoelectron (XPS) spectroscopies.[6] Surface neopentyl moieties were prepared by thermal activation of the C–I bond in adsorbed neopentyl iodide, which, according to our iodine XPS data, occurs around 140 K.[7] The TPD spectra shown in Figure 1 indicate that those neopentyl moieties are quite stable on the surface, mainly because of their inability to follow β-hydride elimination reactions.[3-5,8,9] A fraction of those groups does hydrogenate to form neopentane below 200 K, but the remaining surface fragments decompose only above 350 K to yield isobutene.

The identity of the high-temperature desorbing product was confirmed by performing two additional types of experiments. First, the relative TPD signal intensities of several ion fragments were measured simultaneously in a single experiment and compared with those from mass spectra of the possible products taken under the same conditions. The left frame of Figure 2 shows that the peaks for 41, 39, 56, and 55 amu display the same intensity ratios as those in the mass spectrum of isobutene, and that the signals for 71, 57, or 43 amu are negligible, indicating that no neopentyl iodide, neopentane, isobutane, or any other heavier hydrocarbons are produced in detectable amounts in this case. In addition, a second test was performed using a low ionization energy (22.5 eV) in order simplify the spectra by reducing the probability for molecular fragmentation of the gaseous species in the mass spectrometer; the data displayed in the right panel of Figure 2 confirm the conclusion that isobutene is indeed the main desorbing product in the 400 K feature.

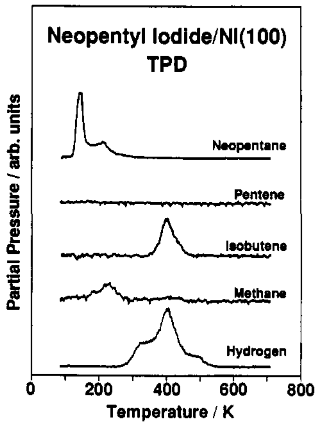

Figure 1. Neopentane, pentene, isobutene, methane, and hydrogen thermal programmed desorption (TPD) data from 6 L of neopentyl iodide adsorbed on a Ni(100) single crystal surface.

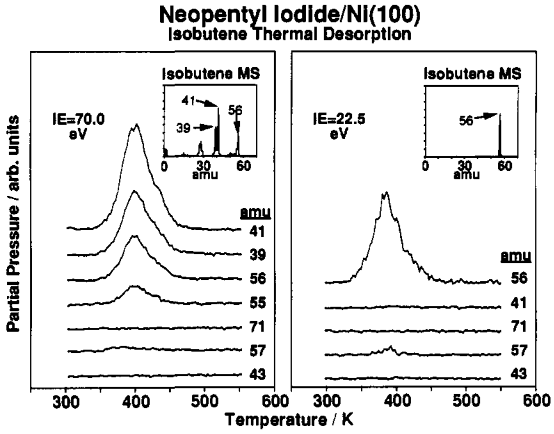

Figure 2. Detailed isobutene TPD traces for neopentyl iodide decomposition on Ni(100) using both 70.0 (left) and 22.5 eV (right) mass spectrometer ionization energies. Mass spectra recorded for the gaseous olefin under the same experimental conditions are provided in the insets for comparison.

The TPD results reported above also indicate that the activation barrier for the overall formation and desorption of isobutene from neopentyl decomposition is of the order of 22 ± 2 kcal/mol.[10-12] Furthermore, since isobutene molecular desorption from Ni(100) surfaces occurs below 235 K,[7] the limiting step for the former reaction must involve the scission of the C–C bond on the surface; we suggest a mechanism where neopentyl groups loose a methyl group from the central atom (the β position). This is perhaps the simplest and most logical mechanism that explains our results, but it should be pointed out that an alternative pathway could nevertheless be proposed in which the cleavage of the α-CC bond is followed by β-hydride elimination of the resulting isopropyl group; isotopic labeling experiments are under way in our laboratory to try to differentiate between these two options.

The activation energy calculated here for the β-methyl elimination is to be contrasted with values for β-hydride elimination (about 10 kcal/mol for alkyl iodide on Ni(100)[7,9] and 13 kcal/mol for ethyl iodide on Pt(111),[13] α-hydride elimination (less than 10 kcal/mol for methyl iodide on either Ni(100)[14] or Pt(111),[15] and C–C coupling (15–18 kcal/mol on Cu(110)[16] and on Ag(111);[17] given the higher energy required for the methyl abstraction, it is not surprising that such reaction can only be seen after blocking some of the other possible

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decomposition pathways. Both α-hydride elimination and C–C coupling reactions seem to be inhibited in the neopentyl/nickel case by steric effects, and direct alkyl radical formation is not expected to take place because of the strengths of the metal–carbon bonds in these systems, which are on the order of 30–40 kcal/mol.[3,15,16,18]

There are very few examples of alkane C–C bond cleavage in the organometallic literature, presumably because these reactions are kinetically limited and therefore compete unfavorably with other pathways.[19–23] Recent work has suggested that C–C bond breaking may also occur on aluminum surfaces,[24] but, to the best of our knowledge, no other direct evidence for β-alkyl elimination from unstrained alkyl species has been reported for any other transition-metal system.

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