Journal of Physical Organic Chemistry

Received: 9 January 2008, Revised: 15 February 2008, Accepted: 26 February 2008,

(www.interscience.wiley.com) DOI 10.1002/poc.1366

Activation of double and triple bonds in C_6 unsaturated hydrocarbons by the Ru(001) surface: an overview

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The decomposition patterns of hexene and hexyne isomers on clean Ru(001), under ultra-high vacuum, are overviewed and correlated with functionality and isomerism. The key surface intermediates and products were identified by reflection absorption infrared spectroscopy (RAIRS). The results evidence the relevant role of the unsaturation position over its nature. The effects of steric hindrance and geometrical isomerism are apparent only in the inhibition of some decomposition pathways. The RAIRS data show that 1-hexene chemisorbs at low temperature (∼90 K) and coverage as a di-σ complex, whereas 1-hexyne forms a di-σ/π complex. By thermal activation, both these species dehydrogenate (in C1), yielding hexylidyne [μ_3-η^1-$C(CH_2)_4CH_3$], which further decomposes (at 280–290 K) into surface metallocycles, [$Ru_3{\equiv}C(CH_2)_4CH_2$-Ru] and [$Ru_3{\equiv}C(CH_2)_4C{\equiv}Ru_3$]. Eventually, at 300 K, complete C—C bond breaking occurs, yielding just adsorbed methylidyne [μ_3-η^1-CH]. The hexene and hexyne isomers with the unsaturation between secondary carbons may follow two surface-assisted decomposition mechanisms. At low temperatures, they adsorb as the corresponding alkyne di-σ/π complex, which implies a rehybridization of the sp_2 (or sp) carbons with reduction of the bond order, plus, for alkenes, dehydrogenation at the same carbons. These complexes decompose by breaking the CC bonds adjacent to the surface anchors: C1—C2 and C3—C4 in the case of the 2-isomer, yielding methylidyne, ethyne di-σ/π complex [μ_3-η^2-CHCH] and propylidyne [μ_3-η^1-CCH_2CH_3], and C2—C3 and C4—C5 in the 3-isomer, with the formation of the ethyne di-σ/π complex and ethylidyne [μ_3-η^1-CCH_3]. The second decomposition path occurs upon direct adsorption at the reaction temperatures. It involves the scission of the multiple bond, with the formation of shorter chain alkylidynes: propylidyne (for 3-hexyne and Z-3-hexene), ethylidyne and butylidyne [μ_3-η^1-$C(CH_2)_2CH_3$] (for 2-hexyne). The reactivity of Z-2-hexene revealed to be different, since no evidence was found for the second decomposition path. This was ascribed to a reduced accessibility of the double bond to the surface, due to a steric hindrance effect of the alkyl chain. The influence of geometrical isomerism was particularly clear in the decomposition of E-3-hexene, which has a remarkable stability. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: reflection absorption infrared spectroscopy (RAIRS); surface reactions; Ruthenium; Ru(001); hexene; hexyne; thermal decomposition; ultra-high vacuum

INTRODUCTION

The chemistry on solid surfaces is considered crucial in many technological areas, namely the selective synthesis of fine chemicals and pharmaceuticals. Relevant information on the elementary processes involved has been obtained by studying model systems, where organic molecules are adsorbed on clean and well-defined single crystal surfaces.[1] Although such investigations are usually restricted to low gas pressures, the picture that emerges from the reactivity of organic molecules on those surfaces contributes to understand their metal surface-assisted decomposition mechanisms.[2] This is achieved largely by the identification of the species formed at different temperatures and coverages, and of their adsorption geometries and sites. A large number of surface-sensitive spectroscopies and methodologies are currently being used.[3] Although developed several decades ago,[4,5] reflection absorption infrared spectroscopy (RAIRS) is still one of the most widely used in these studies. Its high molecular specificity relies on the strict obedience to the metal surface selection rule (MSSR): only vibrational modes that generate a dynamic dipole with a component perpendicular to the surface are observable.[6] It is, therefore, a particularly useful tool to identify the geometry of adsorbates and to study their reactivity.[1]

The role that unsaturated hydrocarbons play in heterogeneous catalytic processes is the reason for the increasing attention on their chemistry on metal surfaces. On the other hand, on account of the catalytic importance of the very reactive hexagonal close packed Ru(001) surface, an effort has been made to understand the chemical behavior of linear alkenes and alkynes upon adsorption, particularly using vibrational spectroscopy.[7–15] Isolating and detecting intermediates and products formed by carbon–hydrogen and carbon–carbon bond breaking has been

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quite challenging, due to the complexity of the adsorption and reactivity of chemisorbed olefins.[16]

The studies involving alkene molecules on clean Ru(001) relate mostly to small carbon chains (e.g., ethene,[10,11] propene,[10] and 1-butene[12]), and have proven that, at low temperature (~90 K) and coverage, adsorption occurs with formation of di-σ complexes, which imply rehybridization of the olefinic carbons (sp_2 to sp_3) and bonding to two Ru atoms. These complexes decompose by thermal activation, with complete dehydrogenation in C1 and hydrogen migration to C2, yielding the corresponding alkylidyne that bonds to the surface on threefold hollow sites: [μ_3-η^1-$C_nH_{(2n-1)}$]. This reaction occurs at lower temperatures as the chain length increases: at ~250 K for ethene,[10] above 150 K for propene,[10] at ~150 K for 1-butene.[12] Ethylidyne [μ_3-η^1-CCH_3] has C_{3v} local symmetry and its fingerprints in a RAIR spectrum are the symmetric modes of the methyl group: on clean Ru(001), the δ_sCH_3 appears at 1340 cm^{-1} and the ν_sCH_3 at 2887 cm^{-1}.[10,11] For propylidyne [μ_3-η^1-CCH_2CH_3], with C_s local symmetry, the active modes are those with an A′ component, and the most intense bands are assigned to the methyl anti-symmetric modes, $\delta_{as}CH_3$ and $\nu_{as}CH_3$, observed at 1450 and 2963 cm^{-1}, respectively, on clean Ru(001). The propylidyne band at 2928 cm^{-1} has deserved some discussion, both on Ru(001) and on Pt(111), being assigned either to the ν_sCH_2 mode or to $2\delta_{as}CH_3$ in Fermi resonance with ν_sCH_3.[10,17,18] The identification and band assignment of longer alkylidynes is less straightforward, since a mixture of rotational conformers may be obtained.[9,10,17]

The position of the double bond has been shown to affect the chemisorption and decomposition pathway of linear alkenes, as in the case of E-2-butene on Ru(001) and Z-2-butene on Pt(111). The low temperature di-σ complex of E-2-butene dehydrogenates at the carbon atoms bonded to the surface, at 200 K, yielding the 2-butyne di-σ/π complex, without the formation of butylidyne.[13] The same happens for Z-2-butene on Pt(111), but at higher temperatures (between 250 and 300 K),[19] since this surface is less active than Ru(001) in catalyzing dehydrogenation reactions.

The chemisorption trends of alkynes on transition metal surfaces have been also the focus of several experimental studies under ultra-high vacuum conditions, with emphasis on ethyne.[20–27] Depending on the molecule, on the metal surface and on the adsorption conditions, two types of surface complexes may form by non-dissociative chemisorption, differing in the interaction of the π orbitals with the metal surface: the di-σ/di-π complex, involving four metal atoms, and the di-σ/π complex bonded to a threefold site.[9,28] These complexes involve a reduction of the bond order, which implies the rehybridization of the sp carbon atoms to between sp_2 and sp_3, more extensive in the case of the di-σ/di-π species.[28]

The ethyne di-σ/di-π complex [μ_4-η^2-C_2H_2], with C_{2v} local symmetry, is favored for low coverage, while the di-σ/π complex [μ_3-η^2-C_2H_2], with C_s local symmetry, is observed for high coverage.[29,30] However, on clean Ru(001), they may coexist at ~120 K: at low coverage, the ethyne di-σ/di-π complex presents two bands at 2950 and 1120 cm^{-1},[26] (or 2940 and 1135 cm^{-1},[25]) assigned to the νCH and νCC modes, respectively. A conversion to the di-σ/π complex is observed with increasing coverage (identified by the shift of the νCC band to 1260 cm^{-1}), suggesting that the two complexes have relatively similar stability.[26,27] For saturation coverage, the ethyne di-σ/π complex starts to decompose at ~250 K, with the formation of acetylide [μ_3-η^2-CCH] and ethylidyne.[25] When both complexes are co-adsorbed, the decomposition occurs at lower temperatures, the reaction being complete at 350 K, yielding methylidyne [μ_3-η^1-CH] and carbon on the surface.

The available data related to the adsorption and decomposition of longer alkynes, such as propyne[31,32] and 2-butyne,[17,19,33] is much more limited. The studies point to a surface chemistry of the di-σ/π (or di-σ/di-π) complex, formed at low temperature, strongly reliant on the triple bond position. Most relevant is the fact that 1-alkynes decompose with formation of the corresponding alkylidyne, whereas alkynes with the triple bond in secondary carbons may decompose by carbon–carbon bond breaking, yielding shorter alkylidynes.

The results presented and discussed in the present overview were selected from a broad work on the surface chemistry of C_6 unsaturated hydrocarbons on clean Ru(001), based on RAIRS data, in order to attain a global perspective on the role of the functionality, unsaturation position, steric hindrance, and geometrical isomerism.

EXPERIMENTAL

The RAIRS experiments were carried out in an ultra-high vacuum system, with a base pressure of 1×10^{-10} Torr, equipped with standard surface preparation and analysis tools, described in detail elsewhere.[34] The chamber is connected by KBr windows to a Mattson Research Series 1 FTIR spectrometer, through purged optical boxes. In order to detect only *p*-polarized light, a wire-grid polarizer was placed in front of the detector, which is a narrow-band mercury-cadmium telluride (MCT). The polished (001) surface of a ruthenium single crystal, 1 mm thick and 10 mm diameter, was cleaned by several sputtering/annealing cycles (2500 eV Ar^+ ions, for 30 min, followed by a quick anneal to 1200 K), prior to the adsorption studies. To evaluate the cleanliness of the surface, carbon monoxide was adsorbed at 100 K, at saturation coverage. On the clean surface, under these conditions, the νCO mode is observed at 2061 cm^{-1}.[35] Low energy electron diffraction (LEED) spectroscopy was also used to analyze the atom long-range order, and to confirm cleanliness. The LEED patterns of the clean Ru(001) and [Ru(001)-($5\sqrt{3} \times 5\sqrt{3}$)R30-CO] surfaces, obtained with a three-grid rear view LEED optics from SPECS, are shown in Fig. 1.

The RAIR spectra were recorded at 4 cm^{-1} resolution and result from the ratio of 1000 co-added sample scans to the same number of background scans for the clean surface. All the

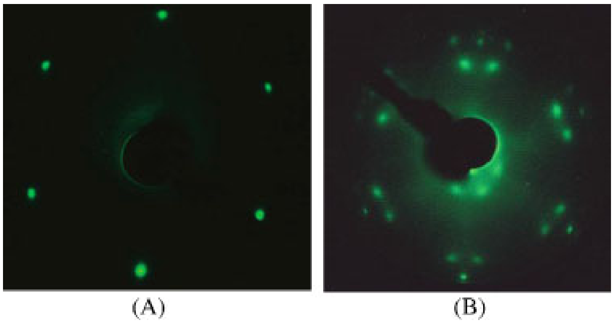

Figure 1. LEED patterns of: (A) the clean hexagonal close-packed Ru(001) surface, obtained at room temperature with 75 eV, and (B) the CO saturated Ru(001) surface [Ru(001)-($5\sqrt{3} \times 5\sqrt{3}$)R30-CO], obtained at 100 K, with 78 eV

molecules (1-hexene, 1-hexyne, 2-hexyne, and E-3-hexene, +99%, from Aldrich; Z-2-hexene +97%, Z-3-hexene +95%, and 3-hexyne 99%, from Fluka) were purified by distillation under vacuum (at 10^{-7} Torr) before use, and were dosed into the chamber through a high precision leak valve. The surface was exposed to the gaseous molecules by backfilling the chamber, with the crystal kept at a constant temperature. The exposures, quoted in units of Langmuir ($1\,L = 10^{-6}$ Torr.s), were not calibrated in absolute values.

RESULTS AND DISCUSSION

Adsorption and thermally activated decomposition of 1-hexene and 1-hexyne

Early RAIRS work on the 1-hexene/clean Ru(001) system led to propose the formation of a di-σ type complex [μ_2-η^2-CH_2CH-$(CH_2)_3CH_3$] upon adsorption of a very low dose (0.025 L) at 90 K. Annealing this sub-monolayer to 100 K promotes complete dehydrogenation of C1 and migration of one hydrogen to C2, yielding some hexylidyne adsorbed on threefold hollow sites, [μ_3-η^1-$C(CH_2)_4CH_3$].[34] Partial decomposition into hexylidyne is also observed by adsorbing at the reaction temperature. For the 1-hexyne/Ru(001) system it was proved that 0.1 L chemisorbs at 100 K by triple bond weakening, yielding a di-σ/π complex [μ_3-η^2-$CHCH(CH_2)_3CH_3$].[36] At 120 K, a reduction of the C1—C2 bond order to 1, with hydrogenation in C2 (probably involving initial hydrogen migration from C1 to C2), yields the same decomposition product as from 1-hexene at 100 K, hexylidyne. The higher formation temperature is explained by the need of a more extensive rehybridization.

The RAIR spectra in Fig. 2(A), (B) refer to the formation and further thermal decomposition of hexylidyne obtained upon adsorption of 1-hexene and 1-hexyne on Ru(001), respectively.

In the RAIR spectrum of 1-hexene adsorbed at 100 K, the absence of modes related to the double bond (as the νC=C, at ~1650 cm^{-1} and the ν=C—H, at ~3070 cm^{-1})[28,37] rules out the hypothesis of physisorption or the presence of π complexes (that would be identified by a νC=C band near 1280 cm^{-1}).[38,39] The bands at 2955 and 1458 cm^{-1} are assigned to the $\nu_{as}CH_3$ and $\delta_{as}CH_3$ modes of the di-σ complex, whereas those at 2878 and 1381 cm^{-1} are assignable to the methyl symmetric modes of surface hexylidyne.[14,34] The shoulder at 2965 cm^{-1} is also related to the $\nu_{as}CH_3$ of this species. Thus, the RAIRS data point to the co-existence of surface species on Ru(001) at 100 K, di-σ complex and hexylidyne, resulting from non-dissociative and dissociative chemisorption, respectively. The observation of both symmetric and anti-symmetric hexylidyne methyl stretching modes may be explained by the presence of different rotational conformers, taking into account the relative flexibility of the alkyl chain.[40] According to the MSSR, conformers with the methyl group pointing laterally must present stronger anti-symmetric CH_3 modes, while those with the methyl group oriented perpendicular to the surface (as the most stable all-*trans*)[41] will show mostly the symmetric modes. The predicted structures of the two more stable hexylidyne conformers (all-*trans* or TTT and *gauche–trans–trans* or GTT) are presented in Fig. 3(A), (B).

Upon sequentially heating the surface up to 120 K, there is a clear increase of the relative intensity of the anti-symmetric methyl-related modes. This indicates that the di-σ complex decomposes predominantly into hexylidyne with *gauche* rotations: at 110 K, only a shoulder in the $\nu_{as}CH_3$ mode assigned to the surface complex remains. The shift to lower wavenumbers of the ν_sCH_3 band may be related to the displacement of the conformational equilibrium toward the formation of *gauche* conformers. This is confirmed by analysis of the methyl deformation region, as an increase in the shoulder at 1472 cm^{-1} (assigned to the $\delta_{as}CH_3$ mode of the GTT conformer) is accompanied by a decrease of the band at 1381 cm^{-1} (assignable to the δ_sCH_3 mode of the TTT conformer).

Between 130 and 290 K, no bands are detected in the RAIR spectra (as shown for 150 K). The absence of bands characteristic

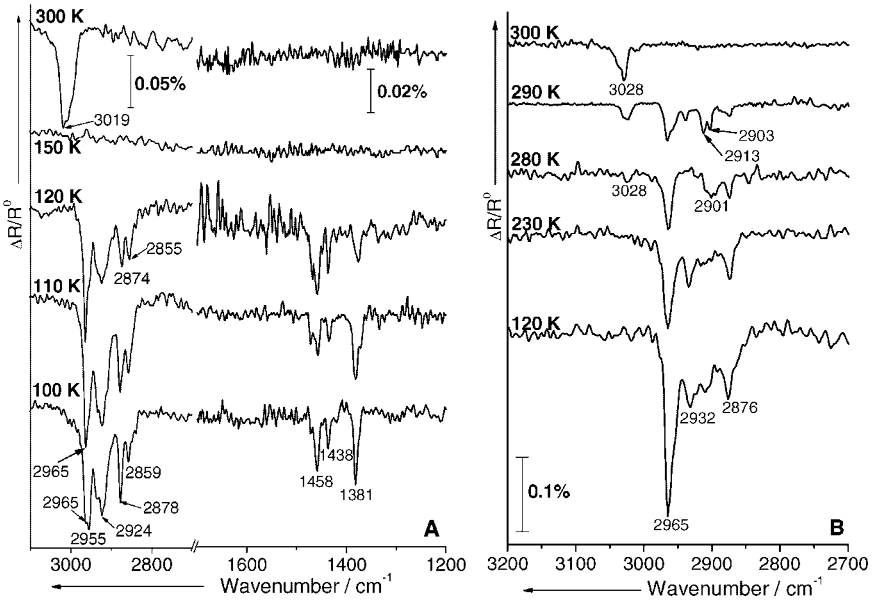

Figure 2. RAIR spectra of (A) 1-hexene (4 L) adsorbed at 100 K, and (B) 1-hexyne (4 L) adsorbed at 120 K, and subsequent annealing to the indicated temperatures. The spectra were scanned at 90 K and baseline corrected

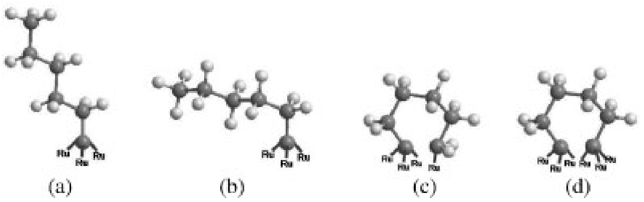

Figure 3. Schematic representation (ball and stick models) of the two more stable rotational conformers of hexylidyne: (a) all-*trans* (TTT) and (b) *gauche-trans-trans* (GTT), and of the metallocycles proposed on hexylidyne decomposition: (c) hydrogenated in C_6 and (d) dehydrogenated. The structures were optimized by energy minimization, using the semi-empirical computation *CS MOPAC Pro* module of *Chem 3D Ultra 8.0.3*

of shorter alkylidynes, namely ethylidyne, or propylidyne, which are stable on Ru(001) at these temperatures, shows that the decomposition pathway of hexylidyne may rather include hydrocarbon fragments whose vibrational modes do not possess a component perpendicular to the surface. Remarkably, annealing to 300 K produces a spectrum with only one large band at 3019 cm^{-1}. It is assigned to the νCH mode of methylidyne adsorbed on threefold hollow sites, [μ_3-η^1-CH], which has a well-characterized fingerprint on metallic surfaces and analogous organometallic compounds.[8,25,42,43] One possible decomposition pathway that accounts for this stable species involves the formation of metallocycles, as proposed to 1-pentene on Pt(111).[42]

The more conclusive results on 1-hexyne adsorbed at 120 K are obtained by analysis of the CH stretching region of the spectra in Fig. 2B. In the deformation region (not shown here), only a band at 1464 cm^{-1} was detected, assignable to the $\delta_{as}CH_3$ mode of the GTT conformer of hexylidyne.[36] The main bands are observed at 2965, 2932, and 2876 cm^{-1}, assigned to the hexylidyne $\nu_{as}CH_3$, $\nu_{as}CH_2$, and ν_sCH_3 modes, respectively. The higher relative intensity of the anti-symmetric modes points to a larger predominance of the GTT conformer than observed for 1-hexene decomposition. This is probably an effect of the higher formation temperature, since apparently conformers with *gauche* rotations are favored as temperature increases. As expected, at 300 K only methylidyne is detected on the surface, through the νCH band, at 3028 cm^{-1}. Nevertheless, essential information on the decomposition mechanism was retrieved by annealing the surface sub-monolayer between 230 and 290 K: methylidyne starts to form at 280 K, and, more important, additional bands are observed at 2901 cm^{-1} (at 280 K), and 2913/2903 cm^{-1} (at 290 K). By comparison with hexylidyne decomposition on Pt(111),[44] these new bands can be related to different metallocycles. The band at 2901 cm^{-1} can be assigned to the ν_sCH_2 mode of a methylene group bonded to the surface, resulting from partial dehydrogenation of the terminal methyl group, with formation of the metallocycle [$Ru_3{\equiv}C{-}(CH_2)_4CH_2{-}Ru$], schematically shown in Fig. 3(c). The doublet at 2913/2903 cm^{-1} is assignable to the $\nu_{as}CH_2$ and ν_sCH_2 modes, respectively, of a more dehydrogenated metallocycle, [$Ru_3{\equiv}C{-}(CH_2)_4C{\equiv}Ru_3$], formed at 290 K. A schematic structure of this metallocycle is shown in Fig. 3(d). The identification of these metallocycles as hexylidyne decomposition products confirms the pathway proposed for 1-hexene. Unfortunately, the deformation region of these spectra was not useful for the discussion, due to miscancellation of water vapor bands that masked the real spectral features.

The comparison between the RAIRS results obtained upon thermal decomposition of 1-hexene and 1-hexyne on clean Ru(001) points to the conclusion that the type of multiple bond is not determining of the reaction mechanism once its position is the same.

Effect of the steric hindrance on the decomposition of 2-hexene and 2-hexyne

The model systems Z-2-hexene/Ru(001) and 2-hexyne/Ru(001) allowed understanding the influence of steric hindrance on the decomposition pathways of long chain unsaturated hydrocarbons. Adsorption studies of Z-2-hexene on clean Ru(001) at 90 K, by RAIRS, led to propose the formation of the di-σ complex [μ_2-η^2-$CH_3HCCH(CH_2)_2CH_3$], in a mixture of rotational conformers.[45] This species results from the π bond breaking with rehybridization of the olefinic carbons. Between 100 and 110 K, the surface species suggested for Z-2-hexene and 2-hexyne decomposition was the di-σ/π complex [μ_3-η^2-$CH_3CC(CH_2)_2CH_3$], that for the alkene implies further dehydrogenation.[45,46] The more relevant RAIRS results on the Z-2-hexene thermal decomposition above 120 K are shown in Fig. 4.

At 120 K, the spectrum is well defined and the bands are sharp, compatible with the formation of a well-ordered layer. The pattern is assignable to the 2-hexyne di-σ/π complex, where the methyl groups originate different bands depending on the position: in C1 it points laterally, and accounts for the $\nu_{as}CH_3$ band at 2955 cm^{-1}, whereas in C_6 it is expected to orient perpendicular to the surface in the more stable conformation, giving rise to the ν_sCH_3 mode, at 2876 cm^{-1}. The corresponding $\delta_{as}CH_3$ (in C1) and δ_sCH_3 (in C_6) modes are observed at 1458 and

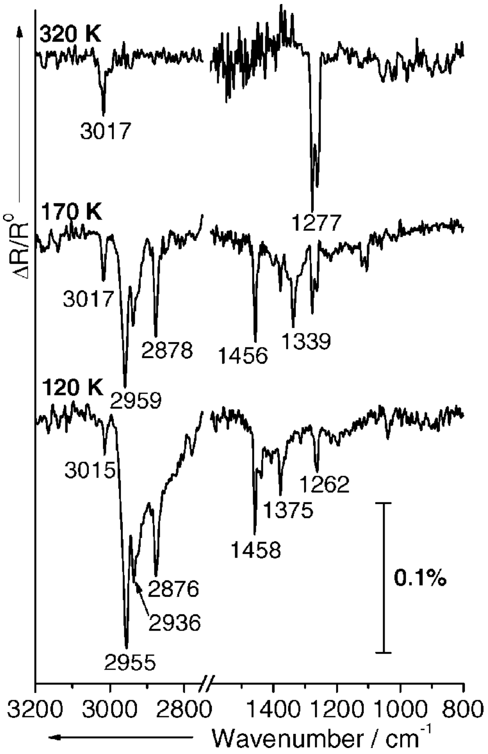

Figure 4. RAIR spectra of Z-2-hexene (4 L) adsorbed on Ru(001) at 120 K, and subsequent annealing to the indicated temperatures. The spectra were scanned at 90 K and baseline corrected

1375 cm^{-1}, respectively. The band at 2936 cm^{-1} is assigned to the $\nu_{as}CH_2$ mode. A more extensive decomposition of some molecules is attested to by characteristic bands of methylidyne and ethyne di-σ/π complex [μ_3-η^2-CHCH], at 3015 and 1262 cm^{-1}, respectively. The band at 1262 cm^{-1} may be assigned to the $\nu C\overset{\cdots}{-}C$ mode of the ethyne di-σ/π complex, and is only observed by RAIRS due to enhancement by charge coupling between the adsorbed acetylene and the metal, resulting in a dynamic dipole perpendicular to the surface associated with the CC stretching.[26] The observation of those decomposition products implies that probably a C_3H_y fragment is also formed. In fact, the shoulder at 1450 cm^{-1} in the band at 1458 cm^{-1} is assignable to the $\delta_{as}CH_3$ mode of propylidyne [μ_3-η^1-CCH_2CH_3], and the one at 2926 cm^{-1} in the 2936 cm^{-1} band may be assigned to the $\nu_{as}CH_2$ mode or to the combination ($2 \times \delta_{as}CH_3 + \nu_{as}CH_3$) of the same species.[10,17] The small band at 1040 cm^{-1} may also be correlated to propylidyne (ρCH_3 mode). Between 120 and 170 K, the di-σ/π complex gradually decomposes without significant differences in the RAIR spectra. In the spectrum obtained at 170 K, the relative intensity of the bands assigned to the di-σ/π complex decrease, while those related with the ethyne di-σ/π complex and methylidyne increase. Accordingly, the observed increase of the ν_sCH_3 mode at 2878 cm^{-1} is explained if this band contains a contribution from another species. In fact, in the deformation region, the new band at 1339 cm^{-1} may be unambiguously assigned to the characteristic methyl umbrella mode of ethylidyne adsorbed on threefold hollow sites, [μ_3-η^1-CCH_3], in C_{3v} local symmetry.[10,17] Adsorbed ethylidyne may result from the hydrogenation of the ethyne di-σ/π complex or from propylidyne decomposition. Since the band related with ethyne (at 1262 cm^{-1}) has relatively increased, the most probable origin of ethylidyne is propylidyne. In fact, decomposition of propylidyne into ethylidyne has been previously observed on Ru(001) at this temperature.[10]

The RAIR spectrum at 320 K shows that the 2-hexyne di-σ/π complex is completely decomposed. Only a methylidyne band (at 3017 cm^{-1}) and a strong doublet at 1262/1277 cm^{-1} are detected, the latter assigned to the ethyne di-σ/π complex on different adsorption sites.[45] The presence of this ethyne complex at such a high temperature may be explained by two consecutive effects: at lower temperatures, an additional stabilization by co-adsorbed species and, at 320 K, the inability to hydrogenate into ethylidyne, since this is already above the hydrogen desorption temperature on Ru(001).[47–49] The alternative assignment of the doublet higher wavenumber component (1277 cm^{-1}) to another decomposition product, such as acetylide [μ_2-η^2-CCH], which has a νCC mode near 1290 cm^{-1},[25] has been ruled out, since both components increase with temperature.

Exposing the Ru(001) surface to 10 L of 2-hexyne, at 100 K, results in a RAIR spectrum with all the characteristic bands of a multilayer.[46] The spectra of the surface species produced upon further annealing are shown in Fig. 5A.

At 110 K, the physically adsorbed 2-hexyne desorbs and the RAIRS spectrum has the characteristic bands of the 2-hexyne di-σ/π complex, namely the modes at 2957 ($\nu_{as}CH_3$), 2936 ($\nu_{as}CH_2$) and 1456 cm^{-1} ($\delta_{as}CH_3$), and the small band at 1317 cm^{-1}, assigned to the $\nu C\overset{\cdots}{-}C$ mode. The strong ν_sCH_3 band, at 2876 cm^{-1}, suggests the presence of a significant amount of *gauche* conformers. The partial further decomposition of this complex results in co-adsorption with other products (as observed for Z-2-hexene at a temperature ~10 K lower): methylidyne is identified by the νCH mode at 3017 cm^{-1}, and the ethyne di-σ/π complex by the $\nu C\overset{\cdots}{-}C$ mode, at ~1260 cm^{-1}.[26] The formation of these products implies C1—C2 and C3—C4 bond breaking, with the possibility of a third fragment, C_3H_x. The more plausible is propylidyne. However, its bands on Ru(001), at 2963, 2928, and 1450 cm^{-1},[10,17,18] are very close to those of the 2-hexyne di-σ/π complex, rendering difficult a clear identification. Its presence is suggested by a shoulder at 2926 cm^{-1} on the $\nu_{as}CH_2$ mode of the di-σ/π complex, assignable to the $\nu_{as}CH_2$ or the ($2 \times \delta_{as}CH_3 + \nu_{as}CH_3$) modes of propylidyne. This species may also be responsible for

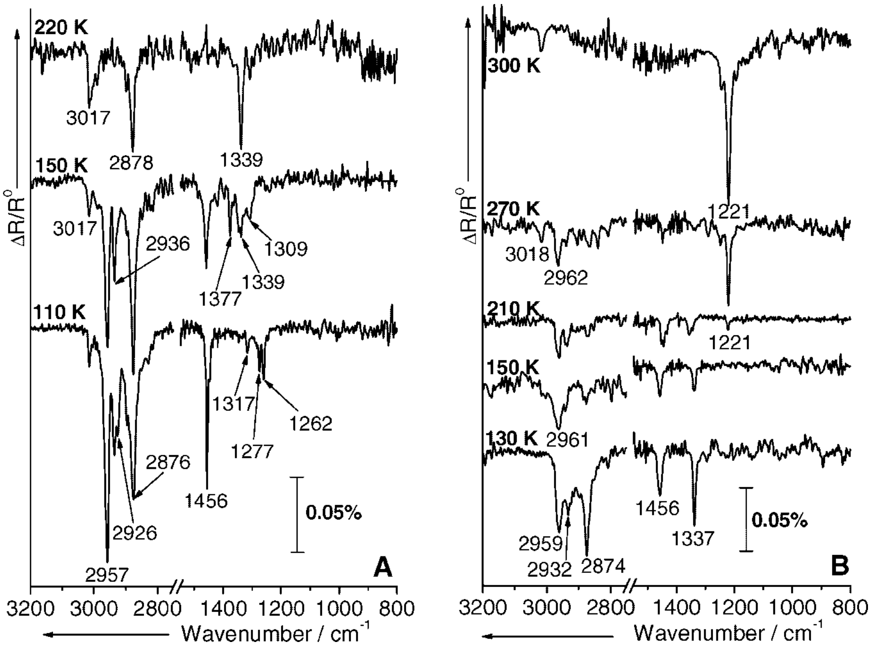

Figure 5. RAIR spectra of 2-hexyne: (A) 10 L adsorbed at 100 K and annealed to the indicated temperatures; (B) 20 L adsorbed at 130 K and subsequent thermal decomposition. The spectra were scanned at 90 K and baseline corrected

the high relative intensity of the $\delta_{as}CH_3$ mode at 1456 cm^{-1}. Ethylidyne, co-adsorbed with the previous decomposition intermediates, is observed at 150 K, identified by the characteristic δ_sCH_3 mode at 1339 cm^{-1}.[11] The two predictable sources for this species are probable, since both the band at ~1260 cm^{-1} and the shoulder at 2926 cm^{-1} are absent. Conformational changes in the 2-hexyne di-σ/π complex with temperature, favoring species with the C_6 methyl group pointing upwards, may explain the appearance of the δ_sCH_3 at 1377 cm^{-1}. The relative intensity of the ν_sCH_3 band increases accordingly, and also due to an ethylidyne contribution. Annealing up to 220 K, only bands related to methylidyne and ethylidyne are observed in the RAIR spectrum, at 3017 cm^{-1} (νCH) and 2878/1340 cm^{-1} (ν_sCH_3/δ_sCH_3), respectively, indicating complete decomposition.

A different RAIRS band pattern is obtained when adsorbing 2-hexyne onto Ru(001) above the decomposition temperature. The spectra obtained after an exposure of 20 L at 130 K and subsequent annealing are shown in Fig. 5B. The C—H stretching region of the spectrum at 130 K compares extremely well with that obtained for 1-butene adsorbed on Ru(001) at 150 K, which results in a mixture of *trans* and *gauche* conformers of butylidyne [μ_3-η^1-C(CH$_2$)$_2$CH$_3$].[12] Therefore, the band at 2959 cm^{-1} is assigned to the $\nu_{as}CH_3$ mode and that at 2932 cm^{-1} to the $\nu_{as}CH_2$ mode (or to the overtone of the $\delta_{as}CH_3$ in Fermi resonance with the ν_sCH_3) of the *gauche* conformer,[12,17] while the band at 2874 cm^{-1}, although very strong, can be assigned to the ν_sCH_3 mode of the *trans* conformer. Concomitantly, ethylidyne is identified by the strong umbrella mode at 1337 cm^{-1}. These RAIRS data point to a decomposition pathway rather different from that observed when adsorbing at low temperature, and imply the C$\equiv$C bond breaking upon adsorption at 130 K.

Annealing the Ru(001) surface to 150 and 210 K, there is a lowering of the integrated intensity across the full spectral range and the CH stretching region becomes less defined. Changes in the layer structure or decomposition of the adsorbed species may explain this progress. At 210 K, the decrease in the bands related with ethylidyne and butylidyne is accompanied by the appearance of a small feature at 1221 cm^{-1}, that increases its relative intensity when annealing to 270 and 300 K. Since butylidyne decomposition on Ru(001) occurs through ethylidyne formation (stable up to at least 300 K),[12] and this new band is not related with that species, this evolution is surprising, and may be justified by an alteration on the stability and reactivity caused by the co-adsorption of ethylidyne and butylidyne. A possible assignment, on group frequency grounds, of the band at 1221 cm^{-1} is to the $\nu C\cdots C$ mode of poorly hydrogenated carbon species (C$_x$H). At 270 K, the presence of methylidyne on the surface is identified by the νCH mode at 3018 cm^{-1}.

Similarly to what was observed for 1-hexene *versus* 1-hexyne adsorption on clean Ru(001), Z-2-hexene, and 2-hexyne undergo the same decomposition mechanism when adsorbed at low temperature (by annealing the di-σ/π complex). However, in the case of 2-hexyne, a second pathway is opened when adsorbing above 130 K (by breaking the CC triple bond), which is inhibited in Z-2-hexene due to the reduced accessibility of the multiple bond.

The influence of geometrical isomerism on the decomposition of 3-hexene isomers and 3-hexyne

The effect of the geometrical isomerism on the decomposition path of C$_6$ alkenes and alkynes was analyzed comparing the model systems 3-hexyne/Ru(001), Z-3-hexene/Ru(001), and E-3-hexene/Ru(001) at different adsorption temperatures and coverages.

Exposing the surface to a very low dose of 3-hexyne, at 100 K, results in non-dissociative chemisorption with rehybridization of C3 and C4, yielding the surface di-σ/π complex, [μ_3-η^2-(CH$_3$CH$_2$)-CC(CH$_2$CH$_3$)]. A multilayer is built at 100 K, for exposures above 1 L.[50] The RAIRS data obtained after adsorbing 3-hexyne at 120 and 240 K are shown in Fig. 6A and B, respectively, as well as the subsequent thermal decomposition.

The RAIR spectrum corresponding to 1 L exposure at 120 K (Fig. 6A) shows typical bands of a 3-hexyne multilayer, at 2976 ($\nu_{as}CH_3$), 2884 (ν_sCH_3), 1375 (δ_sCH_3), and 1327 (ωCH_2) cm^{-1}. The extremely low activity of the C$\equiv$C stretching mode (2214 cm^{-1}) prevents its observation. By annealing to 140 K, the multilayer desorbs, leaving mostly the chemisorbed di-σ/π complex, identified by the $\nu_{as}CH_3$ (at 2967 cm^{-1}), the $\nu_{as}CH_2$ (at 2932 cm^{-1}), and the $\delta_{as}CH_3$ (at 1456 cm^{-1}) modes. The small band observed at 1260 cm^{-1}, which grows with further annealing up to 220 K, shows that decomposition into ethyne di-σ/π complex starts at 140 K, evidencing that C2—C3 and C4—C5 bond breaking occurs. The other possible C$_2$H$_x$ fragments are not detected, probably due to the lack of surface-free sites. Only at 220 K, when just residual hexyne complex remains adsorbed, the characteristic umbrella mode of ethylidyne is observed at 1344 cm^{-1}. The ν_sCH_3 mode, expected at 2880 cm^{-1}, is not well defined. In fact, the entire CH stretching region is broadened, probably due to the contribution of different fragments, namely acetylenic species (with νCH bands at ~2950 cm^{-1}).[25–27]

The RAIR spectrum obtained after adsorption of 3 L of 3-hexyne at 240 K (Fig. 6B) is very different from those at lower temperatures. The absence of bands related with the 3-hexyne di-σ/π complex is clear, and, instead, the pattern is characteristic of a mixed propylidyne/ethylidyne layer. Ethylidyne presents the strongest bands, at 2876 cm^{-1} (ν_sCH_3) and 1344 cm^{-1} (δ_sCH_3). Propylidyne modes are weakly resolved, at 2961 cm^{-1} ($\nu_{as}CH_3$) and 1456 cm^{-1} ($\delta_{as}CH_3$), the νCH_2 mode being even less clear. By successively increasing the surface temperature to 250 and 270 K, the decomposition of propylidyne into ethylidyne proceeds. At 320 K, methylidyne is the only surface species detected (the νCH at 3028 cm^{-1}). The presence of the intermediate propylidyne indicates that the decomposition of 3-hexyne occurs by breaking of the C$\equiv$C bond, ethylidyne being the result of propylidyne decomposition. In fact, direct adsorption of propene on Ru(001) at 230 K yields a mixture of propylidyne and ethylidyne.[10]

In summary, the decomposition of 3-hexyne on Ru(001) may follow two different pathways, depending on the adsorption temperature: below 220 K, by breaking the carbon bonds adjacent to the triple bond, and in the range 220–240 K by triple bond breaking. This behavior is comparable to that of 2-hexyne, although the temperatures are much higher.

The interaction of Z-3-hexene with Ru(001) at low coverage and at 90 K occurs through the formation of a di-σ complex, in a non-dissociative adsorption. Increasing the temperature to 120 K, the surface complex dehydrogenates in the double bond carbons, yielding the di-σ/π complex, and the RAIR spectrum is analogous to that obtained for 3-hexyne at 100 K.[51] This suggests comparable decomposition paths of 3-hexene and 3-hexyne, as was the case for 1-hexene and 1-hexyne. This hypothesis was tested performing a parallel adsorption study of Z-3-hexene at 140 and 220 K. The corresponding RAIRS data are presented in Fig. 7A and B, respectively.

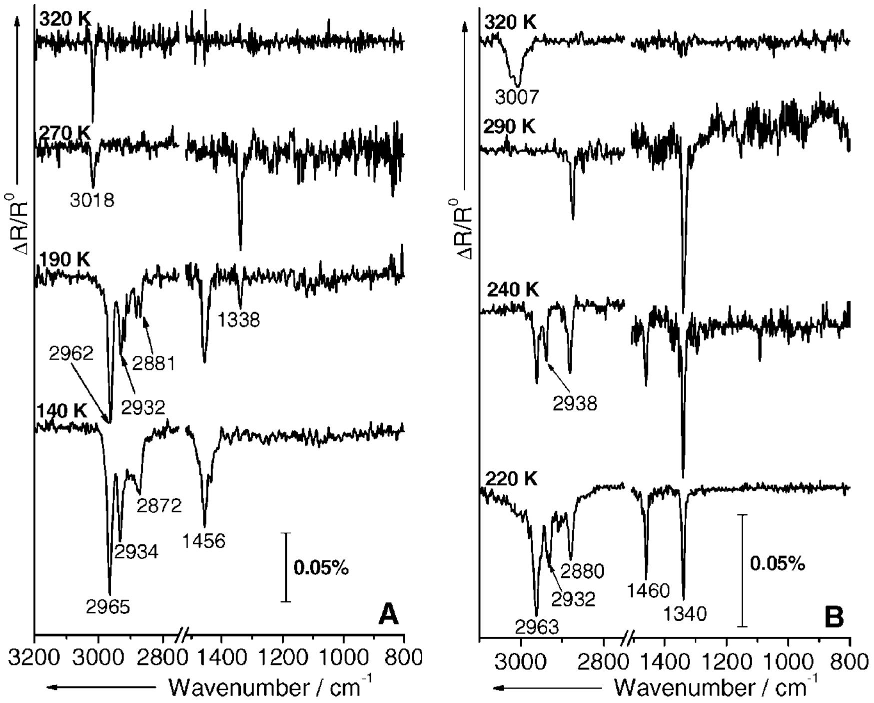

Figure 6. RAIR spectra of 3-hexyne: (A) 1 L adsorbed at 120 K, (B) 3 L adsorbed at 240 K, and subsequent annealing to the indicated temperatures. The spectra were baseline corrected, and were scanned at the adsorption temperatures to avoid re-adsorption upon cooling

By adsorption of 20 L of Z-3-hexene at 140 K, the bands at 2965, 2934, 2872, and 1456 cm^{-1} in the spectrum (Fig. 7A) are clearly assigned to the $\nu_{as}CH_3$, $\nu_{as}CH_2$, ν_sCH_3, and $\delta_{as}CH_3$ modes, respectively, of the chemisorbed di-σ/π complex. The antisymmetric ones are dominant, as expected for this surface complex. No additional bands are detected, indicating that, at this temperature, it is the only species on the surface. The 3-hexyne di-σ/π complex is stable up to 190 K, temperature at which ethylidyne starts to form (δ_sCH_3 mode at 1338 cm^{-1}). At 270 K, the complex has completely decomposed into ethylidyne and methylidyne (νCH mode, at 3018 cm^{-1}). This is the only product identified by RAIRS at 320 K. Comparing with the surface

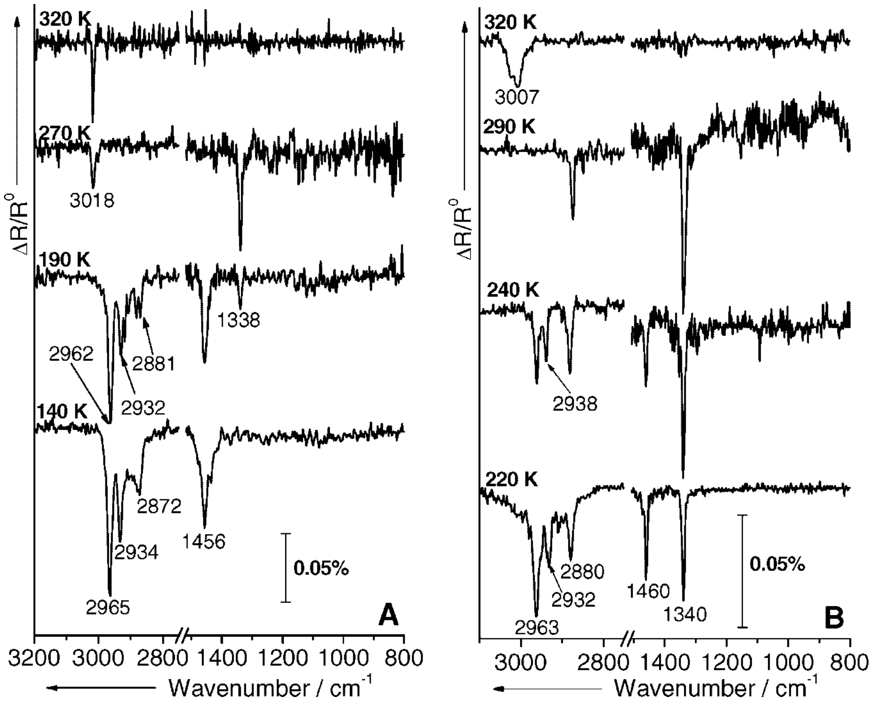

Figure 7. RAIR spectra of Z-3-hexene: (A) 20 L adsorbed at 140 K, and (B) 20 L adsorbed at 220 K, and subsequent annealing to the indicated temperatures. The spectra were scanned at the adsorption temperatures and baseline corrected

species observed for 3-hexyne decomposition by the first mechanism (breaking the C—C bonds adjacent to the surface anchors), only the acetylenic species is not identified. Nevertheless, this does not prove a different decomposition mechanism, since it is well known that the ethyne di-σ/π complex yields ethylidyne when small amounts of hydrogen exist on the surface.[9,29] Since the formation of the di-σ/π complex from Z-3-hexene adsorption implies dehydrogenation, the presence of hydrogen on the surface is probable.

The second decomposition pathway of Z-3-hexene was confirmed by adsorbing at 220 K and by further annealing the surface (Fig. 7B). In the spectrum obtained by direct adsorption at 220 K, the presence of ethylidyne is obvious ($\nu_s CH_3$ at 2880 cm^{-1} and $\delta_s CH_3$ at 1340 cm^{-1}). Breaking the C═C bond implies the formation of propylidyne, which at this temperature decomposes into ethylidyne, as previously discussed. The assignment of the remaining bands to propylidyne can be ambiguous, since they are very close to the ones of the di-σ/π complex formed from Z-3-hexene dehydrogenation. However, the good definition of the bands leads to a better correlation with adsorbed propylidyne: in particular the band at 2932 cm^{-1} ($\nu_{as} CH_2$ mode) is characteristic of its presence on the Ru(001) surface.[10]

Early RAIRS results on the E-3-hexene/Ru(001) system show that this isomer dehydrogenates into 3-hexyne di-σ/π complex only above 140 K.[52] This temperature is ~20 K higher than observed for Z-3-hexene, showing that dehydrogenation is hindered. The RAIR spectra obtained after adsorption of E-3-hexene at 140 and 220 K are shown in Fig. 8A and B, respectively.

When the surface is exposed to 30 L of E-3-hexene at 140 K, the spectrum (Fig. 8A) shows a remarkable difference toward the other isomers studied: there are physisorbed unreacted molecules, identified by the strong γ═CH mode at 968 cm^{-1}. They co-exist on the surface with the first decomposition intermediate yielded by dehydrogenation of the unsaturated carbons, the di-σ/π complex, which can be identified by the $\nu C \overset{\cdots}{-} C$ mode observed at 1290 cm^{-1}. The presence of these two species may be responsible for the splitting of the $\nu_{as} CH_3$ band (2959/2967 cm^{-1}). Surprisingly, after annealing the surface to 170 and 220 K there are still some physisorbed molecules, although co-adsorbed with ethylidyne ($\delta_s CH_3$ mode at 1340 cm^{-1}) and ethyne di-σ/π complex ($\nu C \overset{\cdots}{-} C$ mode at 1277 cm^{-1}). The detection of the latter may be related to a lower amount of hydrogen on the surface, when compared with Z-3-hexene, since a significant part of the adsorbate does not react. It is clear that, with increasing temperature, the relative band intensity of the unreacted molecule decreases, showing that partial decomposition occurs with a pathway comparable to the first one proposed for the Z isomer. However, the reactions are taking place at higher temperatures, evidencing the effect of the geometrical isomerism: the presence of the *trans*-ethyl groups weaken the π bonding to the surface, with the consequent strengthening of the adjacent CC bonds.

E-3-hexene was adsorbed at 220 K, in a tentative to detect a second decomposition mechanism, thus achieving a more thorough comparison between the E and Z isomers. In the spectrum at 220 K (Fig. 8B), unexpectedly, it is obvious that the bands of molecular E-3-hexene appear concomitantly with the $\delta_s CH_3$ mode of ethylidyne, at 1340 cm^{-1}. The occurrence of the second mechanism would involve the double bond breaking upon adsorption, but there is no evidence of propylidyne on the surface (its characteristic νCH_2 mode, at ~2930 cm^{-1}, is absent from the spectrum). These results evidence no more than one decomposition mechanism and a notable stability of E-3-hexene: the non-dissociated molecule is still present on Ru(001) at 240 K and its coverage is eventually reduced only at 280 K. The formation of the 3-hexyne di-σ/π complex by adsorption of the E-isomer at such a high adsorption temperature (220 K) is not

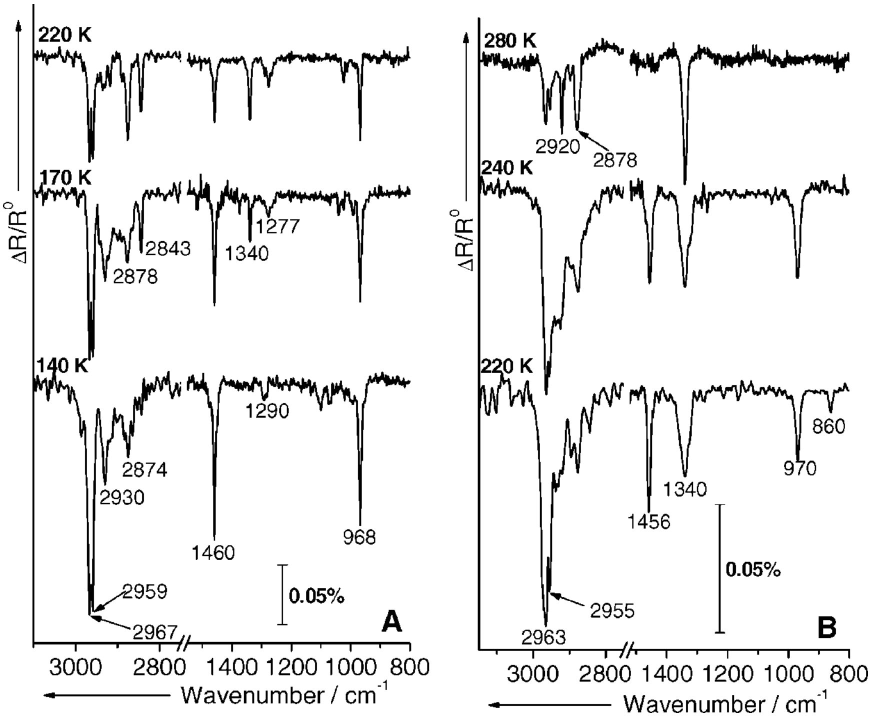

Figure 8. RAIR spectra of E-3-hexene: (A) 30 L adsorbed at 140 K, and (B) 20 L adsorbed at 220 K, and subsequent annealing to the indicated temperatures. The spectra were scanned at the adsorption temperature and baseline corrected

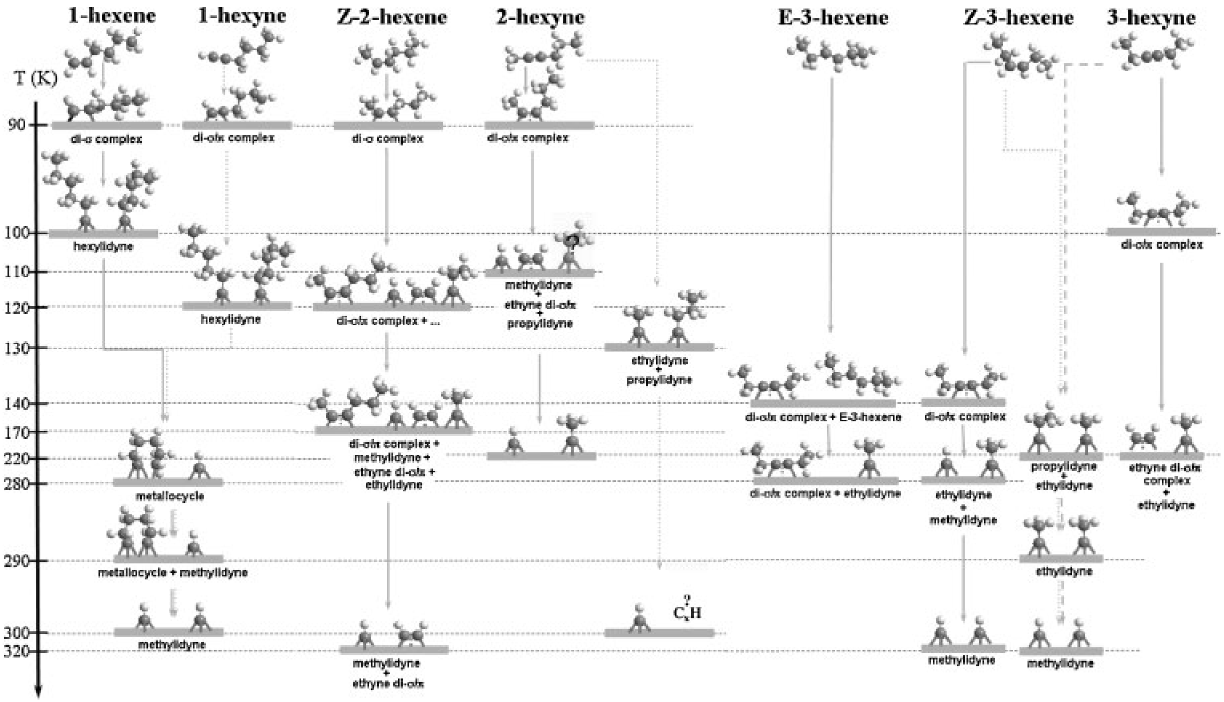

Figure 9. Comparison of the proposed decomposition pathways for hexene and hexyne isomers on clean Ru(001), based on reflection absorption infrared spectroscopy

expected. However, the δ_sCH_3 band of ethylidyne is broader than usual, a possible explanation being the overlap with the $\nu C{\cdots}C$ mode of some di-σ/π complex. Further, indication of its presence is the splitting of the $\nu_{as}CH_3$ band (2963/2955 cm^{-1}), that can be due to rotational conformers of the unreacted E-3-hexene or to the same modes of the di-σ/π complex. This being true, the hexyne complex is stabilized by the large amount of co-adsorbed hexene, unprecedented in previous studies. The band at 2920 cm^{-1}, probably a νCH mode, indicates the presence on the surface of other decomposition products. These may be intermediates of the ethylidyne decomposition (as C_xH_y species), or species more hydrogenated than ethylidyne (such as μ_2-η^1-$CHCH_3$).[9,29] Contrary to what was observed in the decomposition of Z-3-hexene, methylidyne was not identified on the surface up to 280 K. Again, the geometrical isomerism is responsible for the inhibition of the second decomposition mechanism, as the double bond in E-3-hexene is less accessible to the surface upon adsorption.

CONCLUSIONS

Using as model systems hexene and hexyne isomers adsorbed on clean Ru(001) at different temperatures and coverages, it was possible to compare the metal surface-assisted decomposition mechanisms through the identification of the surface intermediates and products, by RAIRS. Three main topics were explored: position *versus* nature of the unsaturation, steric hindrance, and geometrical isomerism.

The compared decomposition pathways of the hexene and hexyne isomers adsorbed on clean Ru(001) are shown in Fig. 9.

It is clear that the position of the double/triple CC bond has a determining effect on the decomposition of C_6 hydrocarbons, independently of its nature. If it involves a primary carbon atom, only one decomposition pathway is observed both for the alkene and the alkyne, via hexylidyne and two metallocycles, eventually yielding methylidyne at room temperature. If the multiple CC bond is between secondary carbon atoms, two decomposition pathways may occur, depending on the adsorption temperature: at low temperature, by breaking the CC bonds adjacent to the anchor carbon atoms of the corresponding di-σ/π complex, leaving the surface ethyne di-σ/π complex plus other C_xH_y fragments; at higher temperatures, by breaking the multiple CC bond, yielding two shorter alkylidynes. The second decomposition mechanism may be inhibited by a steric hindrance effect, as in the case of Z-2-hexene or by geometrical isomerism, as for E-3-hexene. The last effect is also responsible for the relative stability of the E-3-hexene isomer on this surface: whereas molecular Z-3-hexene is only stable below 120 K, E-3-hexene may still be detected at 240 K.

Acknowledgements

This work was supported by Fundação para a Ciência e a Tecnologia (FCT), Project POCI/QUI/60918/2004. The authors acknowledge IN (Instituto de Nanotecnologia e Nanociência).

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