

# Chemistry of 3-Hexyne on Ru(0001): A Reflection–Absorption Infrared Spectroscopy Study

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3-Hexyne has been adsorbed on Ru(0001) at different temperatures under ultrahigh vacuum. At 100 K and very low coverage (0.05 L), the reflection–absorption infrared (RAIR) spectrum is consistent with the formation of a surface di- $\sigma/\pi$  complex involving the rehybridization of the acetylenic carbon atoms. This complex is oriented with the plane containing the  $\alpha$  and  $\beta$  carbon atoms tilted relative to the surface. For an exposure of 0.07 L, a more compact layer of the di- $\sigma/\pi$  species or, alternatively, a second layer of a  $\pi$  complex was identified by the appearance in the RAIR spectrum of the methyl symmetric modes. For higher exposures, a surface multilayer of 3-hexyne is formed, which compares well with the transmission spectrum of solid-phase 3-hexyne. The thermal decomposition of 3-hexyne on Ru(0001) follows two different paths, depending on whether the molecule is chemically bonded to the surface at low temperature (below  $\sim 200$  K) and subsequently heated or adsorbed at higher temperatures, decomposing on adsorption. In the first case, the di- $\sigma/\pi$  complex decomposes above 143 K into an adsorbed acetylenic species and other fragments. These are mostly pumped away, but some dehydrogenates are adsorbed at 223 K as ethylidyne, identified by the small band at  $1344\text{ cm}^{-1}$  assigned to the methyl umbrella mode. In the second case (adsorption at the reaction temperature) the C–C triple bond breaks completely, leaving a mixture of surface species that depends on the temperature. Upon adsorption at 243 K, only adsorbed propylidyne and ethylidyne were identified. At 273 K, the RAIR spectrum is dominated by the intense methyl umbrella mode and, in the C–H stretching region, by the methyl symmetric stretching mode of ethylidyne bonded to the surface in a 3-fold hollow site in  $C_{3v}$  symmetry. Only at 320 K ethylidyne is completely decomposed, leaving adsorbed methylidyne as the only species identified by RAIRS.

## 1. Introduction

The importance of studying the interaction of unsaturated hydrocarbons with metal surfaces is justified by the role that such hydrocarbons play in industrial heterogeneous catalytic processes. In particular, the adsorption and decomposition of small alkynes on metal single-crystal surfaces constitute good models that have been studied over the past 20 years.<sup>1–8</sup> This paper will be concerned with the surface chemistry of a long-chain alkyne (3-hexyne), and therefore, a brief survey of the work published on the chemisorption of shorter alkynes on well-characterized single-crystal surfaces seems convenient.

Ethyne or acetylene adsorption on different metal surfaces has been studied from a theoretical point of view,<sup>7</sup> as well as by several spectroscopic techniques, such as Auger electron spectroscopy,<sup>9</sup> high-resolution electron energy loss spectroscopy (HREELS),<sup>1,2,4,10</sup> thermal desorption spectroscopy (TDS),<sup>4,10</sup> reflection–absorption infrared spectroscopy (RAIRS),<sup>11</sup> and sum frequency generation (SFG).<sup>8</sup> It has been shown that the nondissociative adsorption of acetylene may occur in two forms, differing in the interaction of the  $\pi$  orbitals with the metal surface. They are usually designated by A (or I) or B (or II), depending on the surface and on coverage.<sup>1,4,5</sup> Type A consists of a di- $\sigma/\pi$  complex with four metal atoms ( $\eta^2\text{-}\mu_4\text{-acetylene}$ ) with the HCCH plane oriented perpendicularly to the surface ( $C_{2v}$  local symmetry). Wavenumbers in the range  $1120\text{--}1300\text{ cm}^{-1}$  for the  $\nu(\text{CC})$  mode and  $2890\text{--}2970\text{ cm}^{-1}$  for the  $\nu(\text{CH})$

mode are characteristic of this species.<sup>1,2,5</sup> Type B consists of a di- $\sigma/\pi$  complex bonded to a 3-fold site ( $\eta^2\text{-}\mu_3\text{-acetylene}$ ) with the HCCH plane tilted toward the surface ( $C_s$  local symmetry). In this case, the characteristic wavenumbers of the  $\nu(\text{CC})$  and  $\nu(\text{CH})$  modes are in the range  $1260\text{--}1400$  and  $2930\text{--}3020\text{ cm}^{-1}$ , respectively.<sup>1,5</sup> The frequencies of these modes are highly dependent on the carbon–carbon bond order (the carbon–carbon stretch occurs at  $\sim 2000\text{ cm}^{-1}$  for  $\text{sp}$  hybridization,  $\sim 1600\text{ cm}^{-1}$  for  $\text{sp}^2$ , and  $\sim 1000\text{ cm}^{-1}$  for  $\text{sp}^3$ ). Therefore, in both types of acetylene–metal complexes, there is a carbon rehybridization, the C–C bond order decreasing to a value between 1 and 2. The shift for lower wavenumbers in the di- $\sigma/\pi$  complex suggests a lower carbon–carbon bond order, corresponding to an even more extensive rehybridization, presumably from a greater degree of  $\text{d} \rightarrow \pi^*$  back-donation.

Type A complex has been observed when adsorption occurs at low temperatures on the first-row transition metal surfaces (groups VIII and IB), the exception being made for Ni(110).<sup>1</sup> Type B complex has been detected on Pt(111), Pd(111), Pd(110), Rh(111), and Ni(110)<sup>1,4</sup> and on other second- and third-row transition metal surfaces. The explanation for these differences may be related to the metal–metal distances or to the metal wave functions that participate in forming the molecular orbitals with the adsorbate.<sup>1,4,12</sup>

On Ru(0001) at 120 K, it has been shown by HREELS that acetylene adsorbs as a di- $\sigma/\pi$  species for low coverages, the bands  $\nu(\text{CH})$  and  $\nu(\text{CC})$  appearing,<sup>2,4</sup> respectively, at  $2950$  and  $1120\text{ cm}^{-1}$  or  $2940$  and  $1135\text{ cm}^{-1}$ . When the coverage is

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increased, this species converts to a di- $\sigma/\pi$  complex (identified by the shift of the  $\nu(\text{CC})$  band to  $1260\text{ cm}^{-1}$ ), suggesting that the two complexes have relatively similar stability.<sup>4,10</sup> This transformation is not totally irreversible, since heating a mixed layer of the two complexes to 220 K causes a partial reconversion from di- $\sigma/\pi$  to di- $\sigma/\text{di-}\pi$  complex, explained by a redistribution of islands in a nonuniform coverage.<sup>4</sup>

The thermal decomposition of molecularly adsorbed acetylene on metal surfaces has also drawn a great deal of interest.<sup>2,4,8</sup> On surfaces such as Ni(111)<sup>13</sup> and Fe(110),<sup>14</sup> the di- $\sigma/\text{di-}\pi$  complex seems to undergo carbon-carbon bond breaking, producing methylidyne ( $\equiv\text{CH}$ ). On Pt(111), Pd(111), Pd(100), and Ru(0001), the first dissociation step of the di- $\sigma/\pi$  complex is the carbon-hydrogen bond cleavage, followed by different proposed mechanisms.<sup>2,4,5,8</sup> The overall decomposition may be interpreted in terms of a disproportionation reaction, forming two stable surface intermediates, ethylidyne ( $\text{CCH}_3$ ) and acetylide or ethynyl ( $\text{CCH}$ ). Recently, these intermediate species formed on Pt(111) have been identified by SFG.<sup>8</sup> Ethylidyne was detected on Pt(111) at 356 K<sup>8</sup> and on Ru(0001), which is a more reactive surface, between 230 and 250 K. Near 350 K, it eventually decomposes into methylidyne and carbon atoms.<sup>2</sup>

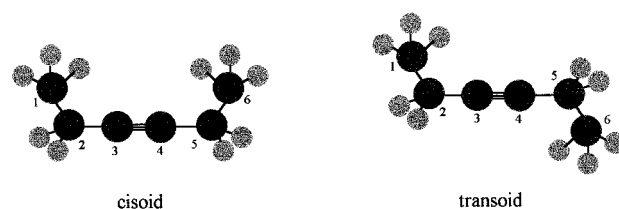
The adsorption of higher alkynes, such as propyne and butyne, has been much less studied. RAIRS studies have shown that the adsorption of propyne on Ni(111) and Cu(110)<sup>6</sup> and on Cu(111),<sup>11</sup> at low temperatures, occurs with the formation of a di- $\sigma/\text{di-}\pi$  complex in a manner similar to that of acetylene. The acetylinic hydrogen and the methyl group are distorted away from the surface. The initial  $\text{C}\equiv\text{C}$  bond lies parallel to the surface, with the bond order much reduced, as indicated by the  $\nu(\text{CH})$  mode, observed at  $2871\text{ cm}^{-1}$  on Ni(111), at  $2751\text{ cm}^{-1}$  on Cu(110),<sup>6</sup> and at  $2855\text{ cm}^{-1}$  on Cu(111),<sup>11</sup> in contrast to the gas-phase wavenumber<sup>15</sup> at  $3320\text{--}3310\text{ cm}^{-1}$ . This complex is stable up to room temperature. On Rh(111),<sup>16</sup> propyne adsorbs nondissociatively at temperatures below 270 K, with the carbon-carbon bond almost parallel to the surface. This species decomposes into different fragments  $\text{C}_x\text{H}_y$  at room temperature and into  $\text{C}_x\text{H}$  fragments above 500 K.<sup>5</sup> Studies with deuterated propyne seem to indicate that the initial carbon-carbon triple bond is the first to break on the surface, forming adsorbed ethylidyne and methylidyne and releasing hydrogen at 330 K.<sup>16</sup>

RAIRS<sup>17</sup> and HREELS<sup>3,18</sup> studies on the adsorption of 2-butyne on Pt(111) have demonstrated that, below room temperature, this molecule also adsorbs nondissociatively as a di- $\sigma/\pi$  complex, with the plane of the carbon atoms tilted with respect to the surface normal ( $C_s$  local symmetry). A different metal-adsorbate bonding is found on Cu(111), since 2-butyne is bonded to four metal atoms as a di- $\sigma/\text{di-}\pi$  complex, with the plane containing the four carbon atoms lying perpendicular to the surface ( $C_{2v}$  local symmetry).<sup>11</sup> This parallelism between the adsorption at low temperatures of acetylene and higher alkynes suggests that the surface chemistry of alkynes is mainly dependent on the carbon-carbon triple bond functionality.

The higher reactivity of Ru(0001) compared to other close-packed surfaces such as Pt(111), and moreover, compared to Cu(111) or Ni(111) toward C-H and C-C bond breaking, has been well documented.<sup>5,16</sup> These studies enable us to predict lower decomposition temperatures for adsorbed alkynes on Ru(0001) than on those metal surfaces. However, to the best of our knowledge, there are no reported studies of alkynes other than that of acetylene on Ru(0001).

It is the purpose of this paper to study the chemistry of a higher alkyne, 3-hexyne, on Ru(0001) by RAIRS. A sample of liquid 3-hexyne at room temperature is probably a mixture of

## SCHEME 1: Conformations of 3-Hexyne



conformers, since rotation is free over the  $\text{C}_2\text{--C}_3$  and  $\text{C}_4\text{--C}_5$  bonds. The two extreme conformations are shown in ball-and-stick models in Scheme 1: cisoid, which belongs to the  $C_{2v}$  symmetry point group, with the  $A_1$  modes allowed by symmetry, and transoid, which belongs to the  $C_{2h}$  symmetry point group, where all modes are allowed except the totally symmetric  $A_g$ .

In the first case, the  $\text{C}\equiv\text{C}$  stretching mode is allowed and gives rise to a weak band at  $\sim 2200\text{ cm}^{-1}$ . In the second, this mode belongs to the totally symmetric  $A_g$  species and is therefore forbidden.

This molecule was adsorbed on Ru(0001) at different temperatures, namely, 100, 123, 223, and 243 K. The coverage effect on the surface species was studied. It has been shown that the decomposition products of 3-hexyne on Ru(0001) depend on the adsorption temperature: when a preadsorbed low-temperature di- $\sigma/\pi$  complex is annealed, the C-C bonds adjacent to the “anchors” break and the species left on the surface are di- $\sigma/\pi$  acetylene and ethylidyne; when adsorption occurs above  $\sim 220\text{ K}$ , the C-C triple bond is the first to break and the surface species formed are propylidyne and/or ethylidyne, depending on temperature.

## 2. Experimental Section

The RAIRS system used in this work consists of an ultrahigh vacuum (UHV) chamber, with base pressure  $2 \times 10^{-10}$  Torr, coupled to a Mattson RS1 mid-infrared spectrometer. It has been described in detail elsewhere, as well as the polish and mount of the Ru(0001) surface.<sup>19</sup> 3-Hexyne was spectroscopic grade (99%) from Fluka and was repeatedly distilled under vacuum before use.

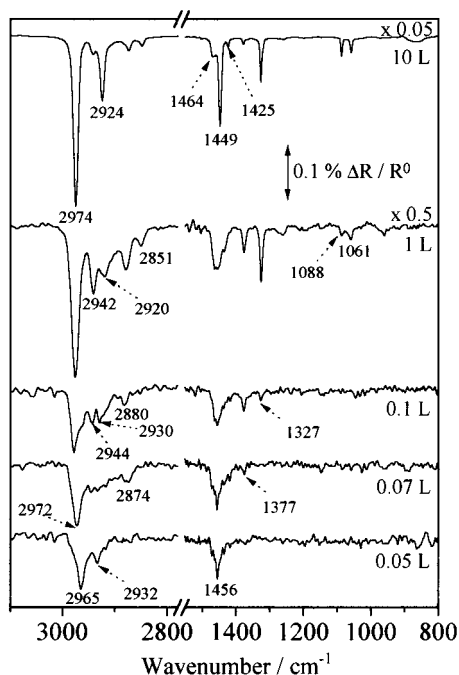
The RAIR spectra were obtained with a resolution of  $4\text{ cm}^{-1}$ , as the result of 1000 co-added scans, and referenced against the background single beam spectra obtained for the clean surface under the same conditions. Only p-polarized light was detected using a wire-grid polarizer placed before the detector, which was a narrow-band MCT from EG&G Judson. Unlike previous studies,<sup>19–21</sup> the spectra were scanned at the adsorption temperature to avoid readsorption upon cooling. The solid-phase 3-hexyne was prepared by freezing a small amount between two KBr plates in liquid nitrogen. The infrared spectrum was obtained in transmission mode, under the same scanning conditions as the RAIR spectra, using as background two clean KBr plates. A wide-band MCT detector from Graseby was used.

## 3. Results and Discussion

**Adsorption at 100 K: Coverage Effect.** The RAIR spectra of 3-hexyne adsorbed on Ru(0001) at 100 K, obtained for different coverages, are shown in Figure 1.

Table 1 summarizes the corresponding band assignments,<sup>22,23</sup> compared to the solid-phase spectrum of 3-hexyne.

By exposure of the Ru(0001) surface to 0.05 L of 3-hexyne at 100 K, only three bands are observed in the RAIR spectrum, one in the C-H deformation region, at  $1456\text{ cm}^{-1}$ , and two in the C-H stretching region, at  $2965$  and  $2932\text{ cm}^{-1}$ . Compared to the solid-phase spectrum, the number of bands is much



**Figure 1.** RAIR spectra of 3-hexyne adsorbed on Ru(0001) at 100 K. Increasing coverages are as indicated.

**TABLE 1: Vibrational Assignments for 3-Hexyne: Solid Phase and Adsorbed on Ru(0001) at 100 K<sup>a</sup>**

solid phase ( $\tilde{\nu}/\text{cm}^{-1}$ )	on Ru(0001) at 100 K ( $\tilde{\nu}/\text{cm}^{-1}$ )					band assignments <sup>22,23</sup>
	0.05 L	0.07 L	0.1 L	1 L	10 L	
2974 (vs)	2965	2972	2978	2976	2974	$\nu_{\text{as}}(\text{CH}_3)$
2942 (s)	2932	2944	2944	2942	2942	$\nu_{\text{as}}(\text{CH}_2)$
2924 (s)		2930	2930	2920	2924	
2874 (s)		2874	2880	2880	2874	$\nu_{\text{s}}(\text{CH}_3)$
2849 (m)				2851	2849	$\nu_{\text{s}}(\text{CH}_2)$
2214 (vw)					2214	$\nu(\text{C}\equiv\text{C})$
1464 (sh)	1456	1456	1456	1456	1464	$\delta_{\text{as}}(\text{CH}_3)$
1450 (m)					1449	
1425 (sh)					1425	$\delta_{\text{s}}(\text{CH}_2)$
1379 (m)		1377	1377	1377	1379	$\delta_{\text{s}}(\text{CH}_3)$
1325 (vs)			1327	1325	1327	$w(\text{CH}_2)$
1143 (w)						$\nu_{\text{as}}(\text{C}-\text{C}\equiv\text{C}-\text{C})$
1088 (m)				1088	1088	$\rho(\text{CH}_3)$
1059 (s)				1061	1059	$\nu(\text{C}-\text{C})$
920 (w)				961		$\nu(\text{C}-\text{C})$
779 (m)						$\rho(\text{CH}_2)$

<sup>a</sup> (vs) very strong; (s) strong; (m) medium; (w) weak; (vw) very weak; (sh) shoulder.

reduced and there are significant shifts (see Table 1). At such low coverage, the lateral interactions between adjacent adsorbed molecules cannot be only responsible for the shifts observed. A nonperturbed physical adsorption of 3-hexyne on Ru(0001) is therefore improbable. We shall compare it with the only alkyne studied on this surface, acetylene,<sup>2,4,5,10</sup> bearing in mind that on other surfaces at low temperatures, propyne and 2-butyne follow the bonding pattern of acetylene.<sup>3,5,6,16</sup> If the same happens on Ru(0001), we may expect the molecule of 3-hexyne to bond nondissociatively as a di- $\sigma$ /di- $\pi$  or as a di- $\sigma$ / $\pi$  species, depending on coverage. In both cases there is a rehybridization of the olefinic carbon atoms, more extensive in the di- $\sigma$ /di- $\pi$  complex, with the consequent reduction of the bond order to a value between 1 and 2. The di- $\sigma$ /di- $\pi$  species is oriented with the plane containing the  $\alpha$  and  $\beta$  carbon atoms perpendicular to the surface (local symmetry  $C_{2v}$ ); the active vibrational modes according to the surface selection rule (which generate dynamic dipoles perpendicular to the surface) would be the methyl

antisymmetric modes and the methylene symmetric and antisymmetric modes. The di- $\sigma$ / $\pi$  species is characterized by a higher bond order between the olefinic carbons, with the plane containing the  $\alpha$  and  $\beta$  carbons tilted relative to the surface ( $C_s$  local symmetry); although not forbidden, the symmetric modes of the methylene groups would generate smaller dynamic dipoles perpendicular to the surface. Accordingly, we assign the band at  $1456\text{ cm}^{-1}$  to the methyl antisymmetric deformation mode, the one at  $2965\text{ cm}^{-1}$  to the methyl antisymmetric stretching mode, and finally, the band at  $2932\text{ cm}^{-1}$  to the methylene antisymmetric stretching mode of a di- $\sigma$ / $\pi$  complex.

Increasing the exposure to 0.07 L produced a spectrum with growing  $\text{CH}_3$  symmetric modes at  $1377$  and  $2874\text{ cm}^{-1}$  (a broad band). A visible split in the broad antisymmetric  $\text{CH}_2$  stretching bands ( $2944$  and  $2930\text{ cm}^{-1}$ ) and a shift to  $2972\text{ cm}^{-1}$  of the antisymmetric methyl stretch are also observed. These changes with increasing coverage suggest that, for a more packed monolayer, there may be a rearrangement of the di- $\sigma$ / $\pi$  species toward gauche conformers (possible by rotation about the  $\text{C}_2-\text{C}_3$  and  $\text{C}_4-\text{C}_5$  bonds). Alternatively, they can indicate that a second layer is building up, still with preferential orientation but less perturbed by the surface, such as a type  $\pi$  adsorbed species.<sup>24</sup>

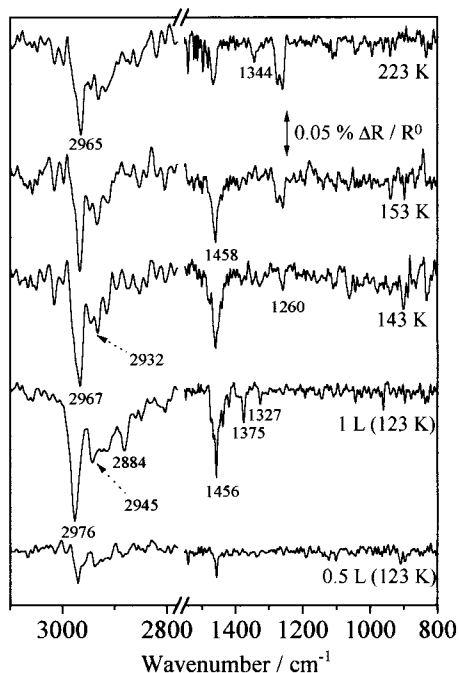
A clear second layer of 3-hexyne is formed upon increasing the exposure to 0.1 L, shown by the gain in intensity of the strongest symmetric mode of methylene (the scissors mode, at  $1425\text{ cm}^{-1}$ ). However, only for higher coverages (i.e., 1 L and above) all the features of a multilayer are observed, namely, the  $\nu(\text{CC})$  modes (at  $1061$  and  $961\text{ cm}^{-1}$ ) and the symmetric stretching mode of  $\text{CH}_2$  groups (at  $2851\text{ cm}^{-1}$ ). The spectrum obtained for an exposure of 10 L includes all the significant bands in the solid-phase spectrum, indicating that a multilayer has been formed (see Table 1).

The band assigned to the  $\text{C}\equiv\text{C}$  stretch has been of no use in this discussion, as even in the 3-hexyne conformer where the mode is symmetry-allowed (cisoid), the corresponding band is very weak. In the RAIR spectra it is hardly detected, even for a multilayer.

**Adsorption at 123 K and Thermal Decomposition.** Figure 2 contains the RAIR spectra obtained upon adsorption of 3-hexyne, keeping the Ru crystal at 123 K. After an exposure of 0.5 L, the spectrum resembles the one obtained for a 0.05 L exposure at 100 K, indicating that at this temperature the di- $\sigma$ / $\pi$  complex is still stable. However, the amount of surface species is lower, which may be explained by the decrease of the sticking coefficient with temperature. By coverage increase to 1 L, a spectrum similar to that of the solid phase is obtained, showing that the multilayer is also stable at this temperature.

After this surface is annealed to 143 K for a few minutes and cooled back to 123 K, the RAIR spectrum becomes simpler: the main bands are the characteristic of the di- $\sigma$ / $\pi$  species, with the  $\nu_{\text{as}}(\text{CH}_3)$  shifted to  $2967\text{ cm}^{-1}$  (closer to the corresponding wavenumber observed at 100 K). Apparently, the top layers were desorbed by annealing, leaving only the chemisorbed 3-hexyne. Additionally, a small band appears at  $1260\text{ cm}^{-1}$  and grows with further heating of the surface to 153 K. It may be assigned to the  $\nu(\text{CC})$  of an acetylenic di- $\sigma$ / $\pi$  species<sup>2,4</sup> left on the surface as a consequence of some decomposition. This band may be enhanced, since charge coupling between the adsorbed acetylene and the metal may result in a substantial dynamic dipole perpendicular to the surface associated with the CC stretching vibration. Simultaneously, an intensity decrease of the bands assigned to the di- $\sigma$ / $\pi$  complex of 3-hexyne is observed. This evolution suggests that, beyond 143 K, the





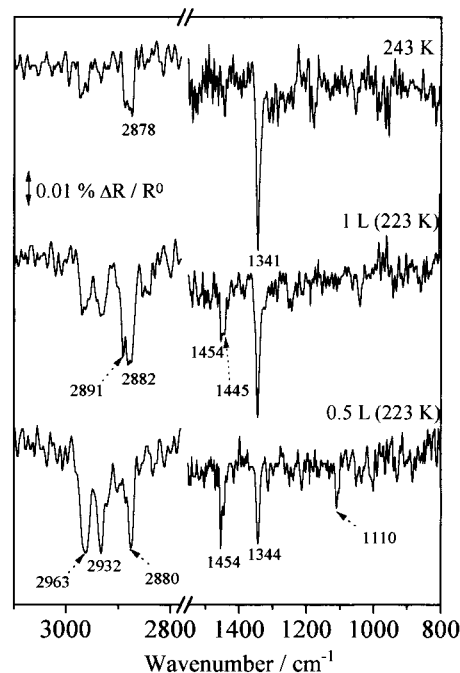
**Figure 2.** RAIR spectra of 3-hexyne adsorbed on Ru(0001) at 123 K. The surface exposed to 1 L was further annealed to the temperatures stated.

3-hexyne di- $\sigma/\pi$  complex starts decomposing on the surface, leaving di- $\sigma/\pi$  acetylene, the other fragments apparently being pumped away because of the high occupancy of the surface.

After subsequent annealing to 223 K, the bands characteristic of the 3-hexyne di- $\sigma/\pi$  complex continue to decrease, although some complex is still present at this temperature. The fingerprint region of the RAIR spectrum is affected by water vapor miscalculation. Nevertheless, it is clear that the band at 1260  $\text{cm}^{-1}$  increases. A new small band at 1344  $\text{cm}^{-1}$  is identified, which may unambiguously be assigned to the umbrella mode of a methyl group pointing upward, although the weaker corresponding stretch is not clearly defined. This suggests that, as decomposition of the chemisorbed 3-hexyne proceeds, some of the fragments other than acetylene are also adsorbed on the surface, possibly on the vacancies left by the initial complex. The CH stretching region is broadened probably because of the contribution of the  $\nu(\text{CH})$  bands of the acetylenic species<sup>2,4,10</sup> at  $\sim 2950 \text{ cm}^{-1}$ .

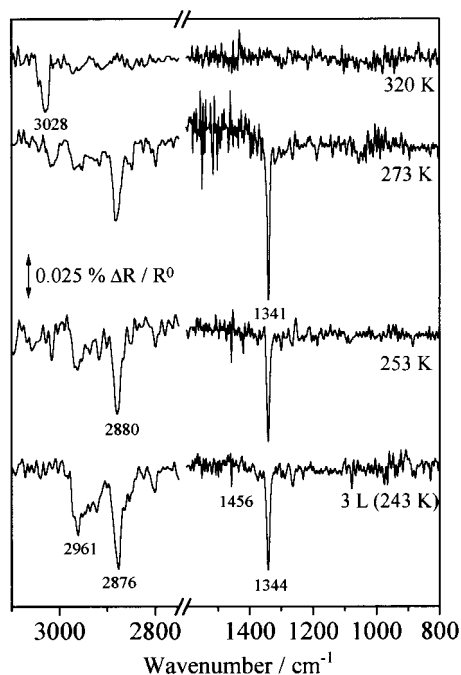
In summary, the spectra in Figure 2 indicate that a multilayer of 3-hexyne on Ru(0001) is stable up to  $\sim 123 \text{ K}$ . At 143 K, some decomposition of the di- $\sigma/\pi$  complex formed upon adsorption at low temperature occurs by breaking of the  $\text{C}_\alpha\text{--C}_\beta$  bonds. The surface species detected at 223 K are residual chemisorbed 3-hexyne, di- $\sigma/\pi$  acetylene, and another decomposition product identified by the symmetric methyl deformation mode. At this point, it may be assigned either to adsorbed methyl (observed on Ru(0001) by decomposition of  $\text{CH}_3\text{I}$ <sup>25</sup> and  $\text{CH}_3\text{--Br}$ <sup>26</sup>) or to ethylidyne in a  $\text{C}_{3v}$  symmetry<sup>27–31</sup> (observed as a stable product of acetylene decomposition on Ru(0001) at  $\sim 230 \text{ K}$ <sup>2</sup> and at  $250 \text{ K}$ <sup>10</sup>). The first assignment, however, is not convincing, since  $\text{--CH}_3$  adsorbed on Ru(0001) is known to dehydrogenate into  $\text{CH}_2$  at  $220 \text{ K}$ .<sup>26</sup>

**Adsorption at 223 K and Thermal Decomposition.** In an attempt to confirm these results, 3-hexyne was adsorbed, keeping the crystal temperature at 223 K. The corresponding RAIR spectra (which are much weaker than the previously obtained) are shown in Figure 3. For an exposure of 0.5 L, the bands at 2963, 2932, and 1454  $\text{cm}^{-1}$ , although a little shifted from



**Figure 3.** RAIR spectra of 3-hexyne adsorbed on Ru(0001) at 223 K. The surface exposed to 1 L was further annealed to 243 K.

previous spectra, can be related to some di- $\sigma/\pi$  complex of 3-hexyne adsorbed without decomposing. Relatively strong bands are also observed at 1344 and 2880  $\text{cm}^{-1}$ , respectively assigned to the symmetric methyl deformation and stretching modes of ethylidyne. A weaker band at 1110  $\text{cm}^{-1}$  may be accordingly, assigned to the C–C stretch of the same species adsorbed on a 3-fold hollow site, which has been well characterized on Ru(0001) by RAIRS, HREELS, and static SIMS.<sup>27–29</sup> More striking is the absence of the band previously observed at 1260  $\text{cm}^{-1}$ , related to adsorbed acetylene. The reason for this fact must reside on the experimental procedure. In fact, the spectrum at 223 K in Figure 2 was obtained by successively annealing a 1 L layer of a di- $\sigma/\pi$  species, bonded to the surface by the acetylenic carbon atoms. With thermal activation, the adjacent C–C bonds may break, some of the fragments dehydrogenating and being re-adsorbed as ethylidyne on probably the few sites left available. The other fragments may be pumped after recombination with hydrogen. In the spectrum under analysis, the surface was exposed to 0.5 L at the reaction temperature (223 K) and, therefore, ethylidyne has been formed upon adsorption. Returning to the assignment of the bands at 2963, 2932, and 1454  $\text{cm}^{-1}$ , not only are they a little shifted from previous di- $\sigma/\pi$  spectra, but the band related to the  $\text{CH}_2$  stretching mode (at 2932  $\text{cm}^{-1}$ ) is surprisingly narrow and its relative intensity toward the methyl modes high. On the other hand, these three bands compare well with those observed upon adsorption of propene on Ru(0001) at 150 K, assigned to propylidyne ( $\text{C}\equiv\text{C--CH}_2\text{--CH}_3$ ), adsorbed on a 3-fold hollow site, with  $\text{C}_s$  symmetry.<sup>27</sup> In this case, the band at 2932  $\text{cm}^{-1}$  may be due to an overlap of the  $\nu_{\text{as}}(\text{CH}_2)$  of the di- $\sigma/\pi$  complex of 3-hexyne with a propylidyne vibration (either the  $\nu_s\text{CH}_2$  or the overtone of the  $\delta_{\text{as}}(\text{CH}_3)$  enhanced by Fermi resonance with the  $\nu_s(\text{CH}_3)$  mode). The formation of propylidyne would imply the breaking of the triple C–C bond of 3-hexyne adsorbed at 223 K. This is not surprising, since a comparative study on propyne and deuterated propyne adsorbed on Rh(111) at 310 K had already shown that the triple C–C bond is the first to break on that surface.<sup>16</sup> The presence of ethylidyne modes suggests a partial decomposition of propylidyne, which is known

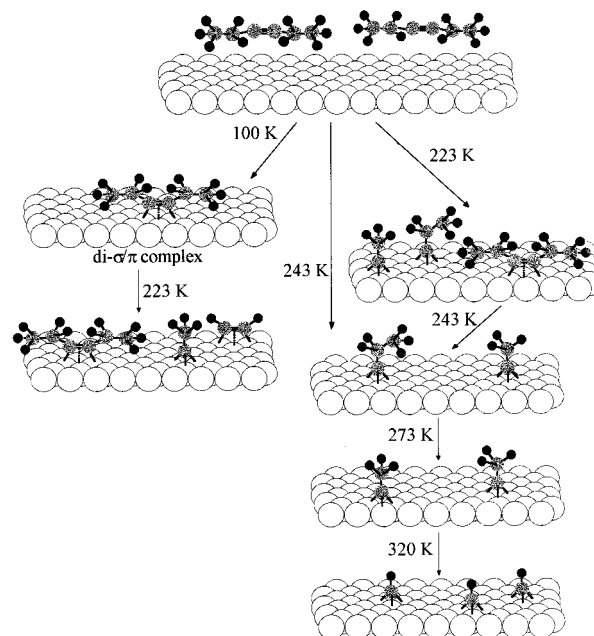


**Figure 4.** RAIR spectra of 3 L of 3-hexyne adsorbed on Ru(0001) at 243 K, further annealed to the temperatures stated.

to occur on Ru(0001) at this temperature.<sup>27</sup> These results lead us to propose that when adsorption occurs at 223 K, part of the 3-hexyne molecules adsorb as a di- $\sigma/\pi$  complex, while others readily decompose into a mixture of propylidyne and ethylidyne. By increasing coverage to 1 L at constant temperature, only the ethylidyne modes grow significantly, while the others decrease. Apparently, the effect of the newly adsorbed molecules at this temperature is to catalyze the decomposition into ethylidyne. The absence of the  $\nu(\text{CC})$  mode, the splitting of the  $\nu_s(\text{CH}_3)$ , and the shoulder in the  $\delta_s(\text{CH}_3)$  suggest that the mixed layer now obtained is not well ordered and that the C—C bonds are not well oriented perpendicularly to the surface. The intensity of the umbrella mode of ethylidyne clearly increases by annealing this adlayer to 243 K. Simultaneously, the propylidyne and di- $\sigma/\pi$  modes become much weaker, indicating that decomposition into ethylidyne is in progress at this temperature.

**Adsorption at 243 K and Thermal Decomposition.** Dosing 3 L of 3-hexyne into the chamber, while keeping the crystal at 243 K, produced a RAIR spectrum compatible with a mixture of propylidyne and ethylidyne, richer in the last species (Figure 4). The strongest bands in the spectrum are assigned to the  $\nu_s(\text{CH}_3)$  and the  $\delta_s(\text{CH}_3)$  of ethylidyne, but poorly resolved modes of propylidyne are also present. Further decomposition of propylidyne into ethylidyne was achieved by successively annealing to 253 and 273 K for a few minutes and then cooling to 243 K to record the spectra. The umbrella mode of ethylidyne reaches maximum intensity for 273 K. With further heating, the ethylidyne bands decrease, showing that it started to decompose on the surface. The usual decomposition products of ethylidyne include the species  $\text{C}_2\text{H}$ , namely, CCH (acetylide), which would produce bands at 2960 and 1290  $\text{cm}^{-1}$  assigned to the  $\nu(\text{CH})$  and  $\nu(\text{CC})$  modes, respectively,<sup>5,28</sup> which are not visible in the RAIR spectra. By annealing to 320 K, however, a unique strong band at 3028  $\text{cm}^{-1}$  suggests the presence of adsorbed methylidyne. No residual ethylidyne is left at this temperature. These results agree well with those obtained upon

## SCHEME 2: Proposed Adsorption and Thermal Decomposition Scheme for 3-Hexyne on the Ru(0001) Surface



adsorption of propene on Ru(0001), where a mixture of propylidyne and ethylidyne was observed at 230 K, completely decomposing into ethylidyne at 300 K, which in turn is stable up to 330 K.<sup>27</sup> The reaction temperatures in the present work are somewhat lower probably because of the presence of other decomposition products formed upon adsorption of 3-hexyne. It has been shown before that coadsorbates may alter the reactivity of the Ru(0001) surface by acting as physical site blockers or by modifying the electronic structure of the metal substrate.<sup>21,32</sup>

## 4. Conclusions

The chemistry of 3-hexyne on Ru(0001) has been studied as a function of temperature and coverage by RAIRS. It has been shown that 3-hexyne adsorbs as a di- $\sigma/\pi$  complex at 100 K for very low exposures (0.05 L). Physical adsorption on top of this species has been achieved by increasing exposure. At 1 L, a multilayer is formed, which desorbs by annealing to 143 K. The di- $\sigma/\pi$  complex starts decomposing at this temperature, leaving an adsorbed acetylenic di- $\sigma/\pi$  surface complex. At 223 K, some di- $\sigma/\pi$  is still present on the surface, but a new decomposition product is identified as ethylidyne adsorbed with local symmetry  $C_{3v}$ . By direct adsorption at 223 and 243 K, an apparently different decomposition path occurs involving the breaking of the C—C triple bond with the production of a mixture of propylidyne and ethylidyne on the surface. At 273 K, the decomposition of propylidyne into ethylidyne is complete and a layer of this species was observed on the surface. At 320 K, adsorbed methylidyne was identified by a strong band at 3028  $\text{cm}^{-1}$ . No additional decomposition products were detected by RAIRS.

As a summary of the RAIRS results obtained in this work, a reaction scheme is proposed for 3-hexyne on Ru(0001), as shown in Scheme 2.

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