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Infrared Spectra of Chemisorbed Molecules

III. Hexenes and Hexadiene on Silica-Supported Nickel

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The infrared spectra of three *n*-hexene isomers adsorbed on a hydrogen-covered surface are virtually identical. The GLC analysis of the gas phase showed that isomerization had taken place. Slightly different spectra were obtained when the hexene isomers were adsorbed on a bare surface. On hydrogen addition, an increase in intensity of the spectrum occurred, indicating hydrogenation of the surface species; dehydrogenation took place when the hydrogen was removed.

In the spectrum of adsorbed 1,5-hexadiene CH_3 bands were present, indicating a rearrangement of the molecule and preferential adsorption at the secondary carbon atoms.

If deuterium is admitted to 1-hexene adsorbed on a hydrogen-covered surface in addition to the formation of ν CD bands, the intensity of the ν CH bands increases, indicating a reaction of adsorbed hydrogen atoms with hydrocarbon species. If, on the other hand, hydrogen is added to 1-hexene adsorbed on a deuterium-covered surface, no ν CD bands are observed.

There are no indications for the presence of species attached to the metal surface by π bonds.

1. INTRODUCTION

The infrared spectrum of ethylene adsorbed on various metals has been extensively investigated (*1–5*), but few data on higher unsaturated hydrocarbons have been published. Eischens and Pliskin (*3, 4*) studied the adsorption of butene, pentene and hexene isomers at 35°C on a hydrogen-covered, silica-supported nickel. They argued that if chemisorption is assumed to take place by a two-point contact of carbon atoms belonging to the double bond, the spectra of the chemisorbed positional isomers would differ. The position of the double bond would then determine the relative number of CH_2 and CH_3 groups in the adsorbed species. This means that 1-hexene would have a CH_2/CH_3 ratio of 3:1, provided the terminal CH_2 group in adsorbed 1-hexene is not regarded as a normal methylene group, while 2-hexene and 3-hexene would have a 1:1 ratio. The above-mentioned authors found no significant differences between the spectra of adsorbed 1-hexene, *trans*-2-hexene and *trans*-3-hexene. The conclusion was drawn that due to dehydrogenation the same surface species are formed from each of the hexene isomers and that most of the molecules are adsorbed by attachment of three or more carbon atoms to the surface. The structure of the chemisorbed species would therefore be independent of the position of the double bond in the original hexene. It was also found that no difference existed between the spectra of 1- and 2-butene. From the absence of a distinct band at 2924 cm^{-1} it was concluded that relatively few unstrained CH_2 groups were present, indicating that in some molecules all four carbon atoms were bonded to the surface. Identical spectra were obtained for adsorbed 1- and 2-pentene.

On addition of hydrogen to chemisorbed butenes, pentenes and hexenes it was concluded that in all cases the hydrogenated species were predominantly bonded to the surface by the terminal carbon atom only. The radicals could be dehydrogenated by evacuating at 35°C.

The spectrum of 1-butene adsorbed on a silica-supported nickel catalyst, obtained during adsorption at −78°C, was attributed to an associatively adsorbed species (*6*). On hydrogenation at this temperature, a large amount of *n*-butane was formed and the metal surface was virtually cleared of chemisorbed species. From spectra obtained after chemisorption at 20 or 95°C, Morrow and Sheppard (*6*) concluded that a greater number of carbon–metal bonds were formed than in the case of the low-temperature (−78°C) adsorption and also, like Eischens and Pliskin (*3*, *4*), that some of the chemisorbed C_4-species may be attached to the surface at three or four carbon atoms. On hydrogenation at 20°C, many surface *n*-butyl groups were obtained and only a small amount of *n*-butane was produced. Although there is general agreement between the results of the above approaches, there is nevertheless some difference in regard to the detailed interpretation of the spectra. Eischens and Pliskin (*3*, *4*) assign a band near 2890 cm^{-1} in the initially adsorbed species to a CH stretching vibration in groups of type CMH or CMH_2–CMH, in which M refers to the metal surface. Morrow and Sheppard, however, assign an absorption near 2930 cm^{-1} to the first of these groups.

This paper is concerned with the chemisorption of 1-hexene, a mixture of *cis*- and *trans*-2-hexene, *cis*-3-hexene and 1,5-hexadiene on a silica-supported nickel catalyst. To obtain more information on the hydrogenation–dehydrogenation step of the adsorbed species, this step was studied by substituting deuterium for hydrogen. Some results described in this paper have already been published (*7*).

2. METHODS

A full description of the infrared cell used and the method of preparation of the silica-supported nickel impregnation catalyst has already been given (*5*). All the results, except those for hexadiene, were obtained with the same pressed disc, weighing 31.2 mg and containing 18.7% nickel.

The spectra were run on a Grubb-Parsons GS4 double-beam spectrometer, the scanning speed being usually 1 μm/32 min (spectral slitwidth 9 cm^{-1}).

After reduction (16 hr, 350°C), the catalyst was cooled in hydrogen and the background spectrum recorded. The hydrogen was removed from the cell by evacuating for 5 min down to 5×10^{-5} Torr. Adsorption of the hydrocarbon took place between 4 and 12 Torr for 1.5 hr at room temperature. The gas phase was removed by pumping down to roughly 3×10^{-5} Torr, measured with a McLeod manometer. Subsequently, the spectrum of the adsorbed molecules was recorded. Further reaction was accomplished by admission of 3–12 Torr hydrogen or deuterium. A new spectrum was recorded after removal of the gas phase at a pressure of about 7×10^{-5} Torr.

The GLC analyses were carried out on a column (length 6 m) packed with silver nitrate–benzyl cyanide on Diatoport S; in this way it was possible to separate all hexene isomers and hexane. Deuterium was prepared by passing D_2O vapor over a column packed with zinc dust and heated at 400°C (*8*). In some experiments, commercially available deuterium (Air Liquide) with a purity of 99.4% was used. Further purification was obtained by diffusion through a palladium thimble (Johnson, Matthey and Co., Ltd.).

The samples of 1- and 2-hexene (*cis–trans* ratio 4:1) and 1,5-hexadiene were purchased from Fluka; *cis*-3-hexene was prepared in our Department of Organic Chemistry. All compounds were purified by column chromatography over Al_2O_3.

3. RESULTS

3.1 Spectra of Adsorbed Hexenes and 1,5-Hexadiene

Spectra obtained after 1-hexene had been adsorbed on a hydrogen-covered, silica-supported nickel catalyst are shown in Fig. 1. On hydrogenation, an increase in the total intensity of the spectrum c is observed. After removal of the catalyst from the beam, a recording of the gas phase showed no infrared bands due to hydrocarbons. The spectrum of the adsorbed species, therefore, is not overlapped by any contribution of the

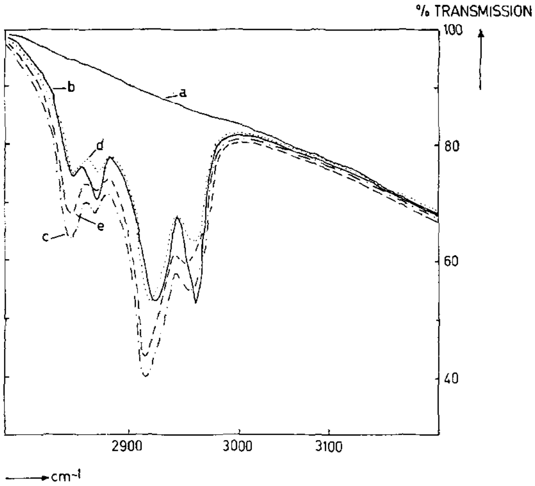

FIG. 1. 1-Hexene adsorbed on a hydrogen-covered surface followed by admission and removal of hydrogen: (a) background, (b) 1-hexene adsorbed, (c) hydrogen admitted, (d) hydrogen pumped off and (e) hydrogen admitted.

gas phase. After pumping for 5 min, a decrease in intensity is observed (spectrum d) and it may be noted that this spectrum is not identical with spectrum b, reflecting a difference in the surface species present before hydrogenation and after dehydrogenation. The intensity of all the bands in spectrum e, recorded after a second admission of hydrogen, is somewhat lower than that in spectrum c, indicating the removal of some adsorbed material in the hydrogenation–dehydrogenation cycle.

The positions of the infrared absorption bands of 1-hexene (Fig. 1) observed in the range studied (2670–3200 cm^{-1}) are reported in Table 1. Two bands in the CH deformation region at 1466 and 1376 cm^{-1} were too weak to be of any use. The position of the four distinct bands agree with the literature (*9*, *10*) values for CH_2 and CH_3 stretching vibrations in nonadsorbed hydrocarbons. We shall use this assignment, made by Fox and Martin (*10*), throughout the text, although the assignment of the CH_3 vibrations has been criticized (*11*).

For the adsorption of ethylene and of higher molecular weight alkenes, Eischens and Pliskin (*3*, *4*) reported considerably different spectra on bare or hydrogen-precovered nickel, whereas Morrow and Sheppard (*2*) and Erkelens and Liefkens (*5*) obtained virtually identical spectra for ethylene under these conditions. The question arose, therefcre, whether the spectrum of adsorbed 1-hexene would be dependent on the presence or absence of hydrogen on the surface. The spectrum of 1-hexene adsorbed on a surface freed from hydrogen by pumping down to 5.5 × 10^{-5} Torr for 2 hr at 350°C is shown in Fig. 2. Contrary to Eischens and Pliskin (*3*, *4*), we did not observe a great difference between the spectrum of 1-hexene adsorbed on a hydrogen-covered or bare surface, except that in the latter experiment the intensity of the $\nu_{as}CH_2$ band was small with respect to the $\nu_{as}CH_3$ band and that the position of the former band was now at 2932 cm^{-1}. When the adsorption time was reduced to 5 min (see Table 2), the intensity of the CH_2 bands was also small with respect to the CH_3 bands. The position of the $\nu_{as}CH_2$ band, however, was unchanged (Table 1).

Spectra of a *cis*- and *trans*-2-hexene mixture and of *cis*-3-hexene adsorbed on a hydrogen-covered surface were almost iden-

TABLE 1
FREQUENCY (cm^{-1}) OF INFRARED BANDS OF 1-HEXENE ADSORBED ON A HYDROGEN-COVERED NICKEL SURFACE, COMPARED WITH LITERATURE DATA (*9*)[a]

Observed				
1-Hexene(b)	$+H_2$(c)	$-H_2$(d)	$+H_2$(e)	Literature
2963	2957	2963	2955	2962 ($\nu_{as}CH_3$)
2926	2918	2920	2918	2926 ($\nu_{as}CH_2$)
2876	2876	2875	2876	2872 ($\nu_{s}CH_3$)
2857	2857	2857	2854	2853 ($\nu_{s}CH_2$)

[a] b, c, d and e refer to the spectra shown in Fig. 1.

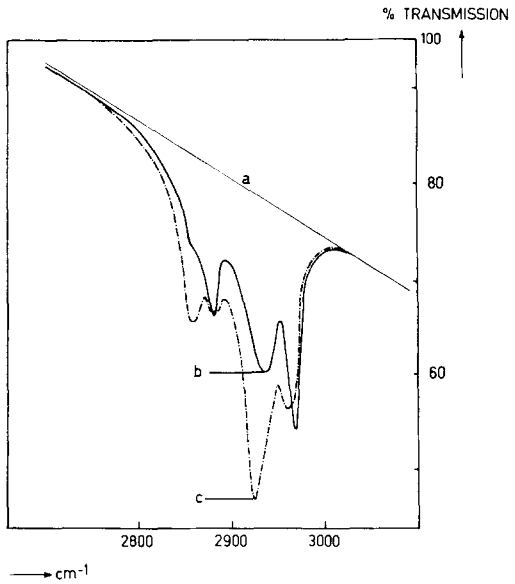

FIG. 2. 1-Hexene adsorbed on a bare surface followed by admission and removal of hydrogen: (a) background, (b) 1-hexene adsorbed and (c) hydrogen admitted.

tical with the spectrum of 1-hexene on such a surface. Also the spectrum of a *cis*- and *trans*-2-hexene mixture adsorbed on a bare nickel surface strongly resembled that of 1-hexene on a bare surface.

The absorbances of all the bands observed are summarized in Table 2. It is clear that in all experiments the intensity of the CH_2 bands of the initially adsorbed species strongly increased on admission of hydrogen, whereas the CH_3 bands hardly varied, causing an increase in the CH_2/CH_3 absorbance ratio (Table 2). After evacuation for 5 min, the intensities of the spectra of the surface species decreased greatly but were almost completely restored after readdition of hydrogen, the CH_2/CH_3 absorbance ratio remaining virtually constant.

Adsorption of the hydrocarbons on the support introduces a small error in the intensity measurements. Therefore, in addition to the experiments with a reduced nickel catalyst, the spectrum of 1-hexene on an unreduced nickel catalyst was recorded after pumping for 15 min at ambient temperature: it was found that the intensity of the spectrum had not changed (Fig. 3) after pumping for 1.5 hr. The absorbances for the $\nu_{as}CH_2$ and CH_3 vibrations were then 0.02 and 0.025, respectively, indicating an uncertainty of roughly 0.1 in the values for the CH_2/CH_3 absorbance ratio shown in Table 2. Likewise, 1-hexene adsorbed on Aerosil could not be removed after pumping for 45 min at 87°C. Its spectrum remained unchanged on hydrogen addition. Nor could hexene adsorbed on Aerosil be removed after pumping for 4 hr at ambient temperature.

When 1,5-hexadiene was adsorbed on a hydrogen-covered nickel surface, νCH_3 bands appeared in the spectrum, obviously indicating a rearrangement of the molecule on the surface (Table 2). The CH_2/CH_3 absorbance ratio was 1.1, which increased to 1.8 on hydrogen admission. This indicates that the compound mentioned behaves in the same way as adsorbed hexenes. The νCH_3 bands also appeared when 1,5-hexadiene was adsorbed on a bare surface. The presence of methyl groups was also observed by Avery (*12*) in 1,3-butadiene adsorbed on a palladium catalyst.

3.2 Analysis of the Gas Phase

The presence of hexene isomers in the gas phase formed by isomerization and desorption during the adsorption period was checked by GLC analysis in some cases. During the adsorption of 1-hexene on a hydrogen-covered surface, *trans*-2-hexene, *cis*-2-hexene and hexane were formed. During the adsorption of *cis*-3-hexene on a hydrogen-covered surface, the following products were formed: 1-hexene, *trans*-2-hexene, *cis*-2-hexene, *trans*-3-hexene and hexane. After removal of the gaseous hydrocarbons by pumping, followed by admission of hydrogen, traces of the latter products were also present (not detectable by infrared spectroscopy). After evacuation and admission of a second dose of hydrogen, traces of lower hydrocarbons were observed in addition to the above-mentioned products, obviously indicating a cleavage of C–C bonds. Since the position of the band due to the CH_2 stretching at the double bond of 1-hexene is at 3080 cm^{-1} and for 2-hexene or 3-hexene at 3020 cm^{-1} (CH stretching), isomerization of 1-hexene adsorbed on a hydrogen-covered surface could also be observed in the spectrum of the gas phase re-

TABLE 2
Absorbance Data for Adsorbed Hexenes and 1,5-Hexadiene[a]

Compound		$\nu_{as}CH_3$	$\nu_{as}CH_2$	ν_sCH_3	ν_sCH_2	$\nu_{as}CH_2/\nu_{as}CH_3$	Surface
1-Hexene	Initial	0.21	0.22	0.12	0.10	1.1	H_2 covered
	$+H_2$	0.20	0.35	0.14	0.17	1.8	
	$-H_2$	0.13	0.23	0.09	0.11	1.7	
	$+H_2$	0.16	0.31	0.11	0.14	1.9	
	Initial	0.17	0.14	0.10	0.06	0.8	H_2 covered[b]
	$+H_2$	0.14	0.27	0.09	0.10	2.0	
	$-H_2$	0.11	0.20	0.06	0.06	1.9	
	$+H_2$	0.13	0.29	0.08	0.10	2.1	
	Initial	0.15	0.12	0.10	—	0.8	bare
	$+H_2$	0.13	0.22	0.08	0.10	1.8	
	$-H_2$	0.07	0.12	0.05	0.05	1.7	
	$+H_2$	0.13	0.24	0.07	0.09	1.8	
2-Hexene (*cis, trans*)	Initial	0.19	0.19	0.11	0.09	1.0	H_2 covered
	$+H_2$	0.20	0.35	0.11	0.16	1.8	
	$-H_2$	0.14	0.25	0.10	0.11	1.8	
	$+H_2$	0.18	0.34	0.12	0.14	1.9	
	Initial	0.13	0.10	0.07	—	0.7	bare
	$+H_2$	0.13	0.21	0.08	0.09	1.6	
	$-H_2$	0.10	0.14	0.06	0.06	1.4	
	$+H_2$	0.12	0.19	0.07	0.08	1.7	
cis-3-Hexene	Initial	0.33	0.32	0.19	0.14	1.0	H_2 covered
	$+H_2$	0.37	0.57	0.21	0.24	1.5	
	$-H_2$	0.27	0.41	0.15	0.16	1.6	
	$+H_2$	0.31	0.50	0.18	0.21	1.6	
	$-H_2$	0.25	0.38	0.15	0.16	1.6	
1,5-Hexadiene	Initial	0.08	0.08	0.05	0.04	1.0	bare
	Initial	0.07	0.07	0.04	—	1.1	H_2 covered
	$+H_2$	0.11	0.19	0.09	—	1.8	

[a] Literature (*9*) assignment.
[b] Adsorption time: 5 min.

corded during the last half hour of the adsorption process. When 1-hexene was adsorbed on a bare or deuterium-covered surface, no change in intensity of the 3080 cm^{-1} band was observed. Nevertheless, traces of the isomers were detected by gas chromatography.

3.3 Deuteration of Adsorbed 1-Hexene

Since the chemisorption of hexene is possibly accompanied by dehydrogenation, it was expected that additional information on the surface reactions of the adsorbed species would be obtained by application of deuterium. In Table 3, the observed bands are compared with literature data (*13–17*) for nonadsorbed hydrocarbons. Bands at 2191 and 2095 cm^{-1} are assigned to ν_{as} and ν_sCD_2 vibrations, respectively. The band at 2212 cm^{-1} may be assigned to the $\nu_{as}CD_3$ or CD_2H vibrations. A further distinction is impossible since no bands due to ν_s at 2075 or 2116 cm^{-1} were observed.

A quantitative interpretation of the

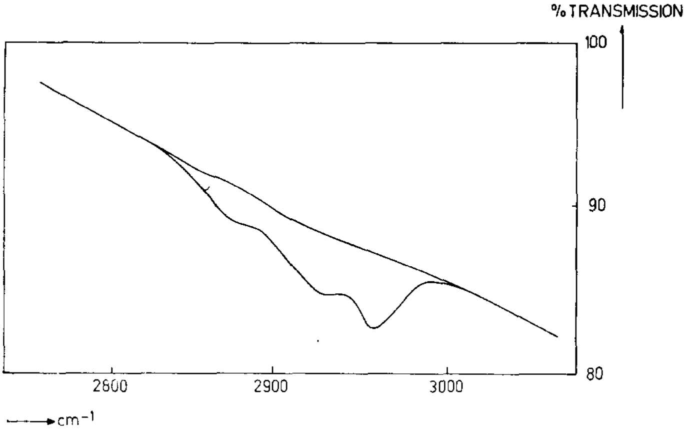

FIG. 3. 1-Hexene adsorbed on a nonreduced nickel catalyst after pumping for 1.5 hr.

spectra in the νCD stretching region is even more difficult than for the νCH region, since intensity data concerning deuterated molecules are scarce. Pine and Steele (*18*) reported that the intensity of the CD vibration increased with increasing electron-donating properties of the substituent. The intensity of the νCD and, of course, also of νCH in the CHD group may therefore very well depend on whether or not the carbon atom of this group is bonded to the surface.

When 1-hexene was adsorbed on a hydrogen-covered surface and deuterium admitted, the intensity of the $\nu_{as}CH_2$ band (2926 cm^{-1}) increased, whereas that of the CH_3 band (2963 cm^{-1}) remained constant. In the νCD region (2000–2200 cm^{-1}), a broad band appeared (Fig. 4). After correction for background, this band was symmetrical with its maximum at 2153 cm^{-1} and was therefore assigned to the νCD in CHD groups (Table 3). Its extreme broadness (obviously indicating that the CHD groups have different environments) is in agreement with measurements by Rohwedder *et al.* (*17*), who also observed broad bands in the spectra of some deuterated methyl stearates. The CHD groups also cause a broad νCH band, overlapped by the other bands in this region. In a parallel experiment, two weak bands at 2190 (CD_2 group) and 2212 cm^{-1} (CHD_2 or CD_3 groups) were also observed. In the latter experiment after the adsorbed

TABLE 3

ASSIGNMENT OF THE BANDS IN THE ν_{CD} REGION

Observed	Literature		
Frequency (cm^{-1})	Frequency (cm^{-1})	Assignment	Ref.
—	2214, 2225	CD_3	(*13*)
2212	2210	CHD_2	(*14*)
2191	2191	CD_2	(*17*)
—	2175-2180	CH_2D	(*14*)
2153	2148	CHD	(*14, 17*)
—	2116	CHD_2	(*14*)
2095	2102	CD_2	(*17*)
—	2075	CD_3	(*13, 14*)

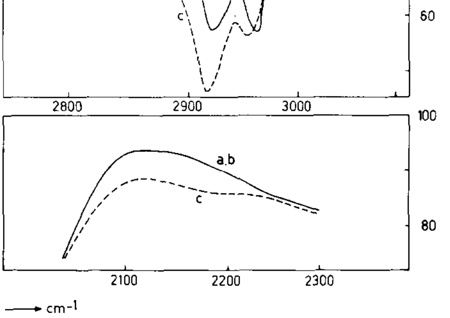

FIG. 4. 1-Hexene adsorbed on a hydrogen-covered surface followed by deuterium admission: (a) background, (b) 1-hexene adsorbed and (c) deuterium admitted.

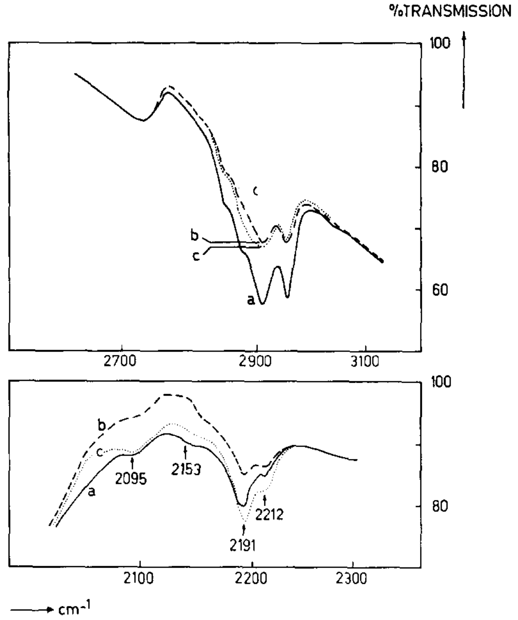

FIG. 5. 1-Hexene adsorbed on a hydrogen-covered surface followed by deuterium admission: (a) 20 hr after deuterium admission, (b) deuterium pumped off and (c) deuterium admitted.

species had reacted with deuterium for 20 hr, an exchange process had taken place, resulting in the formation of additional bands at 2096 and 2153 cm^{-1} (Table 3). As shown in Fig. 5, the bands concerned seem to be superimposed on the broad νCHD band. After removal of the deuterium, the intensity of all bands decreased. Admission of a second dose of deuterium caused the intensity of the various νCD bands to increase, but had little effect on that of the νCH bands. After 20 hr, a slower exchange process had taken place, causing a further intensity increase of the νCD bands.

In connection with this we then studied the adsorption of 1-hexene on a deuterium-covered surface. The catalyst was freed from hydrogen by pumping for 3.5 hr at 350°C, after which it was treated three times at 150°C with deuterium (10 Torr) for 15 min; each treatment was followed by pumping for 5 min. After adsorption of 1-hexene, no νCD bands were observed and the spectrum in the νCH region resembled that of 1-hexene adsorbed on a bare surface (Fig. 2) with regard to the low CH_2/CH_3 absorbance ratio and the position of the $\nu_{as}CH_2$ band (2933 cm^{-1}).

On admission of hydrogen, mainly an increase in the $\nu_{as}CH_2$ band occurred, causing an increase in the CH_2/CH_3 absorbance ratio from 0.82 to 1.85; no bands in the νCD region were observed. After 20 hr, the intensity of the CH bands had increased

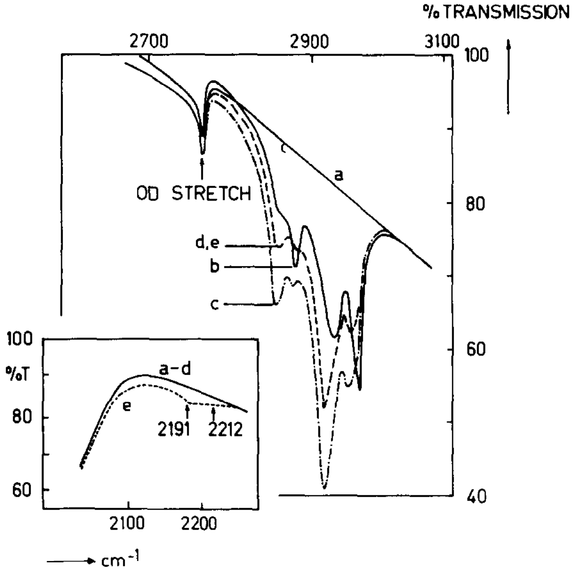

FIG. 6. 1-Hexene adsorbed on a deuterium-covered nickel surface followed by hydrogen admission: (a) background, (b) 1-hexene adsorbed, (c) hydrogen admitted, (d) hydrogen pumped off and (e) deuterium admitted.

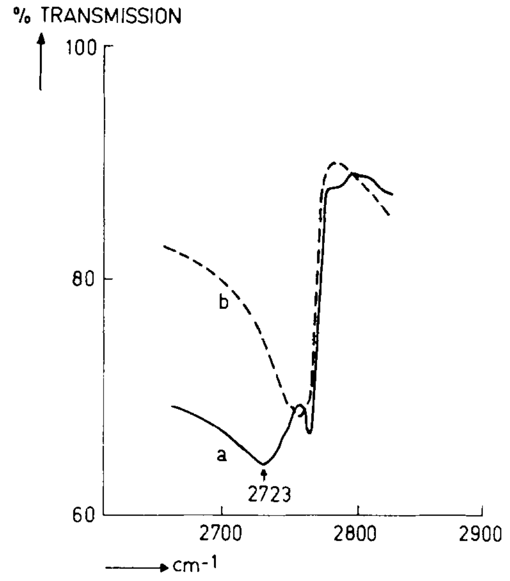

FIG. 7. Disappearance of 2723 cm^{-1} band (interacting surface OD): (a) background, (b) after 1-hexene adsorption.

further. After evacuation of hydrogen and on admission of deuterium, bands were formed at 2191 and 2212 cm^{-1} and an intensity decrease of the νCH bands was observed, this being in agreement with the results of the previous experiment. After replacement of deuterium by hydrogen, an increase in the intensity of the $\nu_{as}CH_2$ band was observed (Fig. 6).

It was also seen that the band at 2723 cm^{-1}, due to the interacting surface OD groups on the silica support, decreased in intensity, obviously indicating exchange with hydrogen atoms formed on the surface by dissociative adsorption of the hydrocarbon molecules. This phenomenon was observed in an experiment in which the surface was treated three times with deuterium (10 Torr) for 10 min at 200°C, followed by 5 min pumping after which a treatment with deuterium (730 Torr) was applied at 350°C for 1 hr (Fig. 7).

The adsorption of 1-hexene was also studied on a nickel surface, from which the hydrogen had been removed by pumping for 17 hr at 350°C (Fig. 8), as well as on a surface precovered with deuterium (Fig. 9). In both experiments, deuterium was admitted to the initially adsorbed hydrocarbon species. A decrease in intensity of the $\nu_{as}CH_3$ band (2963 cm^{-1}), and an increase in intensity and a shift of the position of the $\nu_{as}CH_2$ band (2933 cm^{-1}) took place, while bands at 2095 and 2191 cm^{-1} (CD_2 groups), superimposed on the broad νCHD band, were formed immediately in both experiments. In the latter experiment, the band at 2212 cm^{-1} was also formed.

On removal of the deuterium, an intensity decrease of all bands occurred but admission of a second dose of deuterium again caused an increase in the intensity of the νCD bands followed by a further slow increase. When

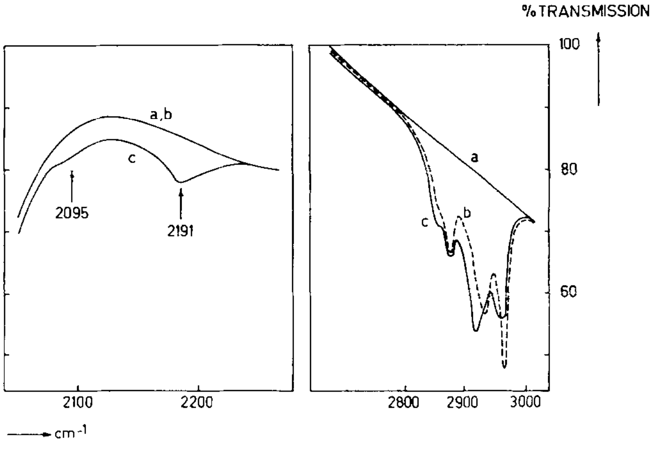

FIG. 8. 1-Hexene adsorbed on a bare nickel surface followed by deuterium admission: (a) background, (b) 1-hexene adsorbed and (c) deuterium admitted.

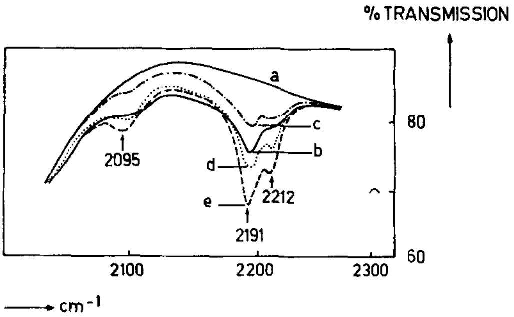

FIG. 9. 1-Hexene adsorbed on a deuterium-covered nickel surface followed by deuterium admission: (a) 1-hexene adsorbed, (b) deuterium admitted, (c) deuterium pumped off, (d) deuterium admitted and (e) after 20 hr.

the deuterium was removed again, the intensity of the νCD_2 bands decreased rather strongly. Hydrogen admission especially increased the intensity of the $\nu_{as}CH_2$ band.

4. DISCUSSION

4.1 Reaction with Hydrogen

Like Eischens and Pliskin (*3*, *4*), we also observed almost identical spectra for the three hexene isomers adsorbed on a hydrogen-covered surface, indicating that practically the same surface species had been formed. However, this observation is not surprising since infrared and GLC analyses of the gas phase after adsorption on a hydrogen-covered surface showed that isomerization had occurred, indicating that a mixture of isomers had in fact been adsorbed. Virtually identical spectra, although different from those mentioned above, were also found when the various hexene isomers were adsorbed on a bare surface or 1-hexene on a deuterium-covered surface, although isomerization of 1-hexene adsorbed on a bare surface was not observed in the spectrum of the gas phase. The structure of the adsorbed species depends therefore not only on the presence or absence of preadsorbed hydrogen, but also on the time of adsorption.

4.1.1 The CH_2/CH_3 Absorbance Ratio

Eischens and Pliskin (*3*, *4*) pointed out that the structure of the adsorbed hydrocarbon may be derived from the ratio of the number of CH_2 and CH_3 groups present. This ratio can, at least in principle, be derived from the CH_2/CH_3 absorbance ratio by comparison with model compounds. Since this method is generally accepted (*19*) we shall use this ratio and comment on it later. Jones (*20*) derived that the CH_2/CH_3 absorbance ratio for nonadsorbed saturated normal hydrocarbons with a CH_2/CH_3 ratio n equals 1.0 ($n = 2$), 1.4 ($n = 3$), 1.8 ($n = 4$) and 2.1 ($n = 5$). From this it would follow that a CH_2/CH_3 absorbance ratio of about 1.0, observed for hexenes and hexadiene adsorbed on a hydrogen-covered nickel surface (Table 2), would point to a CH_2/CH_3 ratio of two or even lower. It may well be that a mixture of surface species is concerned here, preferentially adsorbed at the secondary carbon atoms thus giving rise to a low CH_2/CH_3 ratio by the presence of 2 CH_3 groups/molecule. From the absorbance ratio of 1.8 or 2.0 found (after hydrogen admission) in a number of experiments shown in Table 2, it would follow that the CH_2/CH_3 ratio of the adsorbed species is at least 4, so that the greater part of the surface may then be occupied by species chemisorbed at the terminal CH_2 group only. In the case of hydrogen admission to *cis*, *trans*-2-hexene adsorbed on a bare surface or *cis*-3-hexene adsorbed on a hydrogen-covered surface, the CH_2/CH_3 absorbance ratio is somewhat lower (about 1.6), possibly indicating that in this case more hydrogenated hydrocarbon species were adsorbed at a secondary carbon atom.

In addition to the CH_2/CH_3 ratio, we have to discuss the behavior of the absorbance of the $\nu_{as}CH_2$ vibration near 2926 cm^{-1}. On admission of hydrogen to 1- and 2-hexenes adsorbed on a hydrogen-covered surface, the CH_2-absorbance increases by a factor of 1.6 and 1.8, respectively (Table 2), at an almost constant intensity of the CH_3 band. Assuming that Beer's law is valid, the number of CH_2 groups present in the adsorbed molecule must increase on hydrogen admission by the same factor, indicating that in the initially adsorbed hydrocarbon species on average more than two carbon atoms were attached to the surface. These conclusions are in agreement with those of Eischens and Pliskin, although their arguments were based on the relatively high intensity of the 2890 cm^{-1} band, which we did not observe.

There is, however, one experimental aspect which is difficult to understand when one assumes that the CH_2/CH_3 absorbance ratio, or the intensity of the $\nu_{as}CH_2$, can be used for determining the structure of the adsorbed species. On removal of hydrogen admitted to the initially adsorbed species, the intensity of the CH_3 and CH_2 stretching vibrations (Fig. 1, Table 2) decreases with an almost constant CH_2/CH_3 absorbance ratio. Although dehydrogenation is observed, the spectrum seems to remain consistent with that of an adsorbed *n*-hexyl group, this being contradictory. It is therefore doubtful whether the use of the CH_2/CH_3 absorbance ratio provides a reliable method for elucidating the structure of adsorbed hydrocarbons. This doubt is enhanced by Morrow (*21*), who studied the spectrum of $(Ph_3P)_2Pt(C_6H_{13})_2$ and stated a $\nu_{as}CH_2/CH_3$ absorbance ratio of 1.57 for the hexyl group. This figure is even lower than most values quoted by us for the hydrogenated hexene species (Table 2).

Sheppard and Ward (*19*) point out that surface-attached alkyl groups seem to have a less pronounced minimum between the symmetric and asymmetric CH_2 and CH_3 absorption regions in comparison with nonadsorbed hydrocarbons. The absence of this minimum can also be observed in Fig. 1 and is obviously due to the presence of hidden bands, caused by groups connected to the metal surface, in the spectrum. Such bands seriously affect the possibility of obtaining a correct interpretation of the spectrum.

The previously expressed doubt about the suitability of the CH_2/CH_3 absorbance ratio for elucidating the structure of adsorbed hydrocarbons would therefore appear to be justified. The same doubt is applicable to the use of the intensity of the $\nu_{as}CH_2$ vibration and also to the use of the integrated intensity as a measure of the total number of CH bands present (*19*).

4.1.2 Position of the Bands

It is possible that physical adsorption of the hydrocarbon chain causes the shift in the frequencies of the observed $\nu_{as}CH_2$ and CH_3 bands (Table 1) due to admission of hydrogen. It has been reported (*22, 23*) that in the case of physical adsorption of hydrocarbons, bands shift towards frequencies below those of gaseous molecules. From this and from the data in Table 1 it would follow that the hydrocarbon chain of the hydrogenated species is closer to the surface than it is before hydrogen admission. The mentioned change in νCH frequency towards lower wave numbers on hydrogenation of the initially adsorbed species on palladium was also observed by Avery (*12*) and discussed extensively. It was attributed to an interaction between the C–H dipoles of the adsorbed species and Pd–H dipoles. Avery did not observe a reversible change in the νCH frequencies on pumping, which would be expected if the adsorbed hydrogen is removed. Stephens (*24*) pointed out that a part (3.0 units) of the hydrogen adsorbed on palladium at 0°C and 10^{-2} Torr is loosely attached to it so that it can readily be removed by pumping, although a larger part (4.2 units) is firmly attached to the surface. However, the coverage of the palladium surface at the temperature caused by the infrared beam and under the vacuum conditions applied is not known.

Due to this uncertainty in Avery's interpretation and since no change occurs in the position of the ν_sCH_2 and ν_sCH_3 vibrations on hydrogen admission to adsorbed hexene (Table 1), we believe that a change in the intensity of overlapping bands is the correct explanation.

Another point which calls for explanation is the rather high position (2933 cm^{-1}) of the "CH_2 band" in the spectrum of 1-hexene adsorbed on a bare or deuterium-covered surface. It is possible that the $\nu_{as}MCH_2$ group has a band at that position, although Sheppard and Ward (*19*) assign a band in the region 2920–2895 cm^{-1} to this group. Another possible explanation for the high position of the relevant band may be a high number of CH_3 groups in the adsorbed molecule, if we accept that, contrary to the Fox and Martin (*10*) assignment, the ν_sCH_3 frequency absorbs in the 2910–2940 cm^{-1} region, as was indicated by Winther and Hummel (*11*).

4.2 Deuteration of Adsorbed Species

The formation of the broad band at 2153 cm^{-1} (νCD) obtained after admission of deuterium to 1-hexene adsorbed on a nickel surface precovered with hydrogen points to the formation of –CHD groups from –CHM groups. Therefore, there must also be a broad band in the νCH region. The increase in intensity of the νCH_2 band cannot be explained from the presence of this hidden band, nor by the presence of deuterium atoms in the molecule, since Fig. 5c or 6c shows that an intensity increase of the bands in the νCD region does not entail any change in intensity of the bands in the νCH region. Obviously, adsorbed hydrogen reacts with the adsorbed hydrocarbon species on admission of deuterium.* The results of experiments in which hydrogen was admitted to 1-hexene adsorbed on a nickel surface precovered with deuterium and where no bands in the νCD region were observed, also indicated a preferential reaction of the adsorbed hydrocarbon species with hydrogen. In agreement with our observations it was observed (*25*) that due to a kinetic isotope effect, the hydrogenation of ethylene with hydrogen proceeded faster than with deuterium.

The observed intensity increase of the bands in the νCH region on hydrogen or deuterium admission is obviously caused by a decrease in the degree of dissociation of the CH bonds of the hydrocarbon when the total occupation of hydrogen/deuterium atoms increases. It has indeed been pointed out (*26*) that tightly bonded hydrogen atoms are unable to react with ethylene. When deuterium was admitted to 1-hexene adsorbed on a bare or deuterium-covered surface, a decrease of the $\nu_{as}CH_3$ band occurred, which might point to the formation of species attached to the surface by their terminal carbon atom.

5. CONSEQUENCES FOR NONSPECTROSCOPIC WORK

Galwey and Kemball (*27*) attempted to determine the structure of hydrocarbons dissociatively adsorbed on a reduced and evacuated nickel surface, by replacing the adsorbed dissociated hydrogen atoms by deuterium from the gas phase. It may be concluded from our work that, on deuterium admission, only the hydrogen atoms that have not reacted with the adsorbed hydrocarbon species are exchanged. Therefore stronger dissociation of the hydrocarbon than that measured has presumably taken place.

A second point is the type of bonding of adsorbed hydrocarbons. Adsorbed hexenes appear to be attached to the metal surface by σ bonds rather than by π bonds. This follows from the absence of bands above 3000 cm^{-1}, which were observed in the spectrum of, for instance, propylene platinum chloride (*28*). This finding is in agreement with the work of Morrow and Sheppard (*2*) on ethylene and also with the work of Erkelens and Eggink-Du Burck (*29*) who did not observe the spectrum of a π-complex when benzene was adsorbed on nickel.

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* A referee of this paper has suggested that some of the hydrogen dissociatively cleaved from the alkene is retained in a loose association with the adsorbed alkene and is not readily exchangeable with gaseous deuterium.

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