Infrared Spectra of Olefins Adsorbed on Silica Supported Palladium

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Infrared spectra, primarily in the ν C–H region, were obtained for the adsorption of isobutene, 4,4-dimethyl-1-pentene, 1-pentene, propene, cyclopropane, and 1,3-butadiene on silica supported palladium. The branched chain mono-olefins resulted in intense spectra on initial adsorption which on hydrogenation, were subject to relatively minor intensification and frequency perturbation ($\Delta\nu \sim 5$ cm^{-1}). By contrast, the linear mono-olefins produced weak but well-defined spectra which were subject to considerably greater intensification and frequency perturbation ($\Delta\nu \sim 20$ cm^{-1}) on hydrogenation. Furthermore these olefins were more strongly adsorbed than their counterparts from branched chain mono-olefin adsorption and hydrogenation. This behavior was interpreted by considering that the more strongly adsorbed linear mono-olefins were in more intimate contact with the surface and therefore subjected to greater frequency perturbations by it when hydrogen forms a dipolar monolayer on the surface. The adsorbed species derived from the branched chain mono-olefins are considered to be of the alkyl type whereas the linear mono-olefins are believed to be multiple bonded to the surface at high energy step or ridge sites. This feature allows all the constituent hydrogen of the linear species to be in rapid and reversible equilibrium with a hydrogen atmosphere. Adsorption of 1,3-butadiene produced a completely dehydrogenated residue which was associated with the absence of an alkyl function in the molecule. Hydrogenation of this residue resulted in a strongly adsorbed species apparently composed of polymerized C_{4n} units.

INTRODUCTION

The study of olefins adsorbed on metal surfaces has, for many decades, attracted the attention of surface chemists. Of all the available combinations of metals (of which the Group VIII metals are the most important) and olefins the adsorption of ethylene on nickel has been by far the most widely studied. It is therefore not surprising that with the advent of infrared spectroscopic techniques to study adsorption on metals this system has received the same disproportionate treatment. For example, infrared spectroscopic studies of ethylene on nickel have been reported on

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numerous occasions (1–6) whereas the corresponding studies on palladium (7) and platinum (3, 6) appear with considerably lower frequency.

Since the original work of Pliskin and Eischens (1, 2) where a brief study was made of the adsorption of propene (1), 1-butene and the isomeric hexenes (2) on nickel, the only work on higher olefins appears to be limited to that of Sheppard and co-workers (8) where the adsorption of 1-butene on nickel and platinum (9) has been the most thoroughly studied.

The present study has employed a technique frequently exploited by catalytic chemists, of varying both the geometrical and chemical characteristics of a selection of reactants to probe the modes of adsorption. A preliminary study of a wide range

of olefins on nickel, platinum (10), and palladium showed that adsorption on palladium produced the most striking contrast between the type of olefin adsorbed and the characteristics of the adsorbed species. This paper describes the results of the adsorption on palladium of a selection of olefins which included (i) branched chain mono-olefins, (ii) linear mono-olefins, and (iii) the conjugated diolefin 1,3-butadiene. In this way it was felt that a greater insight was gained about the nature of the adsorbed species without detailed reference to spectroscopic assignments and interpretations.

EXPERIMENTAL METHODS

Cab-O-Sil supported palladium samples were prepared by impregnated Cab-O-Sil (2.0 g) with palladium chloride (0.5 g) dissolved in dilute hydrochloric acid (25 ml). The slurry was dried at 100°C with frequent stirring before grinding into a fine powder. It was found that, if the slurry was not agitated during drying, the palladium chloride concentrated on the slurry–air interface so that subsequent grinding led to an inhomogeneous sample with reduced transmission. It was also apparent that the transmission was enhanced by prolonged grinding of the powder. About 200 mg of this preparation was pressed in a 1-in. diameter die at 2–3 tons for a few minutes. The resulting pellet was mounted in the pellet holder of the infrared cell shown in Fig. 1. The pellet was outgassed *in situ* at 200°C on a conventional high vacuum line for 1–2 hr after which it was cooled to room temperature and the reduction with hydrogen commenced immediately. The pellet was heated to 300–350°C over a period of 30–60 min in a stream of hydrogen (~5 Torr). At this temperature it was occasionally subjected to large static pressures of hydrogen of up to 300 Torr. About 3 hr of this treatment was regarded as sufficient to ensure complete reduction to the metal.

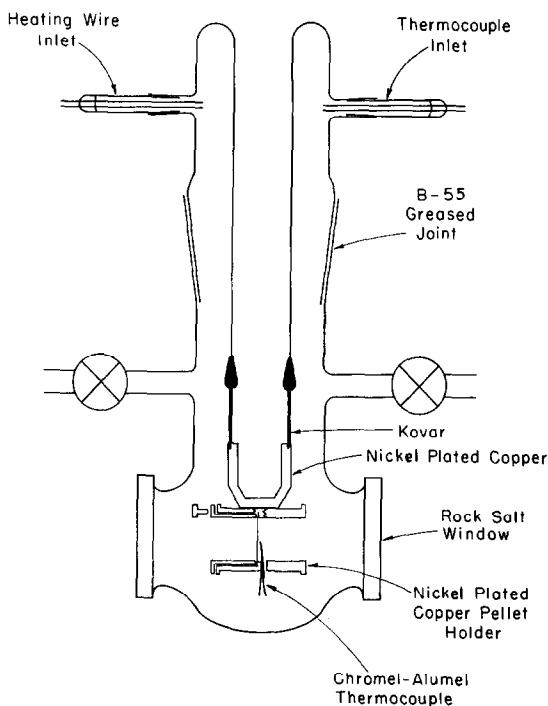An important feature of the infrared cell was the nickel-plated copper pellet holder

FIG. 1. Variable temperature cell used for infrared studies of hydrocarbon adsorbed on silica supported metal pellets.

which was welded to Kovar and hence to the glass Dewar of the cell. The high thermal conductivity of this arrangement allowed the pellet to be cooled with liquid nitrogen from 300 to −100°C in about 5 min. It was found that unless the copper pellet holder was plated with nickel, chemical distillation occurred at 300°C to coat the pellet with a thin layer of metallic copper.

After the pellet was cooled to room temperature in 50 Torr hydrogen, the cell could be evacuated to 10^{-6} Torr in 5 min. About 30 Torr of the desired olefin was then admitted to the cell and allowed to remain in contact with it for at least 12 hr. Evacuation of the gas phase then left only the firmly absorbed species on the metal surface. When open to the vacuum line the cell was at all times protected by traps at liquid nitrogen temperature or alternatively by some suitable refrigerant when condensable vapors were being used. By regenerating the pellet in hydrogen at 300°C it could be used many times without any loss of activity.

Infrared spectra were recorded on a GS2 grating spectrometer usually operated with a spectral slit width of 3–4 cm^{-1}. The low transmission of the palladium pellets was balanced by attenuating the reference beam with a similar pellet in an evacuated cell so that a relatively horizontal base line could usually be obtained. The cell was firmly fixed in the spectrometer with locating blocks and clamps in a manner which both made movement impossible and facilitated the setting up of the cell in the same position from day to day.

Hydrogen, both for the reduction of the pellet and subsequent hydrogenation of the adsorbed species, was prepared by diffusing cylinder hydrogen through an electrically heated palladium–silver alloy thimble. Olefins were Phillips Research Grade obtained from the National Physical Laboratory, Teddington (purity >99.9%) and were further purified by several freeze, pump, thaw cycles before use.

Gas analysis was performed on a Perkin-Elmer F11 gas chromatograph using a 35 ft × ¼ in. column of dimethylsulfolane on Celite operated at 20°C. Quantitative estimates were based on peak area defined as peak height by peak width at half peak height.

RESULTS AND INTERPRETATION

In general, the study of the infrared spectra of adsorbed hydrocarbons was restricted to the region of the C–H stretching vibrational mode (>2800 cm^{-1}). Thus the observed spectra could be used as an index to the number and type of C–H bonds in the adsorbed species. In this way the processes of adsorption, desorption, hydrogenation, and dehydrogenation of the adsorbed species could be conveniently followed.

The surface species produced by the interaction of olefins with palladium can be divided into three categories depending on the type of infrared spectrum observed and its behavior to subsequent hydrogenation and pumping: (a) branched chain mono-olefins, viz, isobutene and 4,4-dimethyl-1-pentene; (b) linear mono-olefins, viz, 1-pentene and propene (cyclopropane gave identical results to propene); and (c) the conjugated diolefin 1,3-butadiene.

(a) **Branched chain mono-olefins.** The pattern of behavior of this class of olefin is exemplified by the spectra obtained after adsorption of isobutene followed by hydrogenation and pumping cycles (Fig. 2). Band centers are also listed in Table 1. The intense spectrum produced after initial evacuation of the gas phase was stable to pumping for up to 30 min. On addition of hydrogen the existing bands were simply broadened and shifted to slightly lower frequencies ($\Delta \nu \sim 5$ cm^{-1} for the band at ~ 2960 cm^{-1}) without substantially altering the optical density of the major band. The increase in intensity of the 2912 cm^{-1} band is attributed largely to a broadening of the dominant 2960 cm^{-1} band. Evacuation of the hydrogen from the cell produced a time dependent decrease in the intensity of the spectrum—for example, after 15 min the optical density of the major band was reduced by about 50%. Some sharpening of the bands also occurred during evacuation as shown by the fact that the rehydrogena-
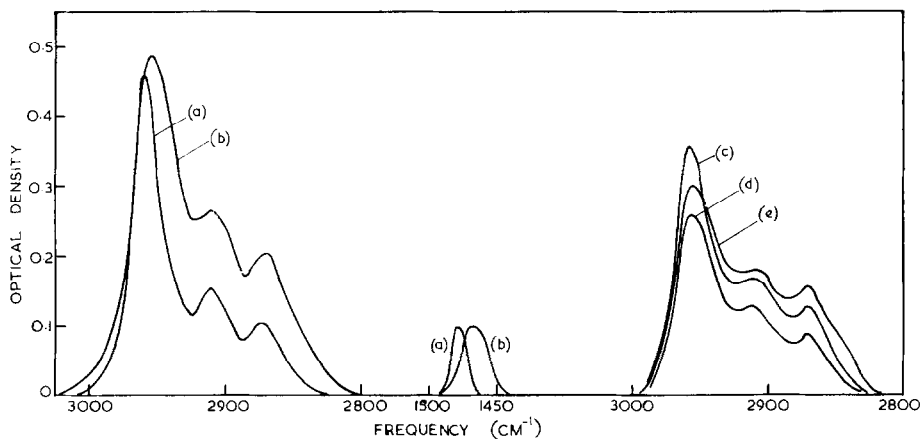
FIG. 2. Infrared spectra of isobutene on palladium at ~20°C after the following successive operations: (a) ~12-hr contact followed by 5-min pumping; (b) addition of hydrogen (50 Torr); (c) pumping for 4 min; (d) pumping for 15 min; and (e) pumping for 18 min followed by re-addition of hydrogen (50 Torr).

tion served mainly to broaden the bands, again without greatly increasing the optical density of the major band. Thus, for this type of adsorbed species desorption rather than extensive dehydrogenation occurred on pumping. Continuation of these pump–hydrogenation cycles reduced the intensity of the spectrum even further.

The spectral behavior of 4,4-dimethyl-1-pentene on palladium to the usual pump–hydrogenation cycles was similar to that observed for isobutene except that the surface species was more readily removed by pumping after initial hydrogenation (Fig. 3 and Table 1).

The distinguishing features of the adsorbed species produced from this class of olefin were:

(i) intense spectra in the ν C–H region of saturated hydrocarbons (<3000 cm^{-1}) after initial contact of the olefin

(ii) relatively minor intensification and perturbation of the bands to lower frequencies on initial hydrogenation, and

(iii) the relative ease of desorption of the hydrogenated species by repeated pump–hydrogenation cycles.

(b) **Linear mono-olefins.** The spectra observed after adsorption of 1-pentene on palladium followed by the usual hydrogenation and pump cycles are shown in Fig. 4. Band centers are also recorded in Table 1. Prolonged pumping did not affect the initial spectrum (Fig. 4a). On admission of hydrogen a large increase in intensity occurred which was accompanied by a broadening and shift of the major band at 2967 cm^{-1} to a considerably lower frequency, viz 2945 cm^{-1}. A relatively stronger band at 2912 cm^{-1} was also produced. A band in the δ C–H region was also detected at 1460 cm^{-1}. Evacuation of

TABLE 1

FREQUENCIES OF THE ν C—H BANDS PRODUCED BY ADSORPTION AND HYDROGENATION OF OLEFINS ON PALLADIUM

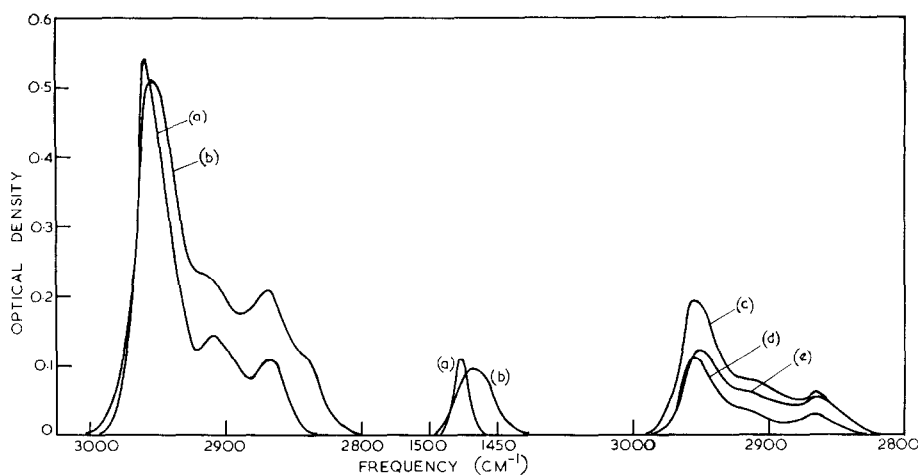| Olefin	After evacuation of the hydrocarbon gas phase					After hydrogenation			
Isobutene		2960	2912	2872		2955	2910	2871	
4,4-Dimethyl-1-pentene		2960	2910	2871		2955	2910[a]	2871	
1-Pentene	3020	2968	2920[a]	2880		2945	2912	2880[a]	2850[a]
Propene, Cyclopropane		2960	2920	2880	2860	2945	2912	2880[a]	2850[a]
1,3-Butadiene						2960[a]	2912	2874	2855

[a] Broad or weak ill-defined bands.

FIG. 3. Infrared spectra of 4,4-dimethyl-1-pentene on palladium at ~20°C after the same successive operation described for isobutene (Fig. 2).

the hydrogen from the cell reduced the intensity of both the ν C–H and δ C–H bands to zero within a few seconds. Rehydrogenation produced a spectrum (Fig. 4d) similar to that observed after the initial hydrogenation but with an overall reduction in intensity and a relative intensification of the 2912 cm^{-1} compared with the 2945 cm^{-1} band. Subsequent pumping and rehydrogenation merely reproduced the spectra depicted in Figure 4c and d, respectively, without any decrease in intensity of the fully hydrogenated species and clearly

represents the dehydrogenation and hydrogenation of a firmly chemisorbed species. Furthermore, this species was stable to heating in hydrogen and brief pumping at temperature up to 80°C, which was the upper limit studied.

The spectra of adsorbed propene following the usual pump–hydrogenation cycles are illustrated in Fig. 5 and band centers are recorded in Table 1. While the general behavior of these species was similar to that observed for 1-pentene some small differences are self-evident. Over the same
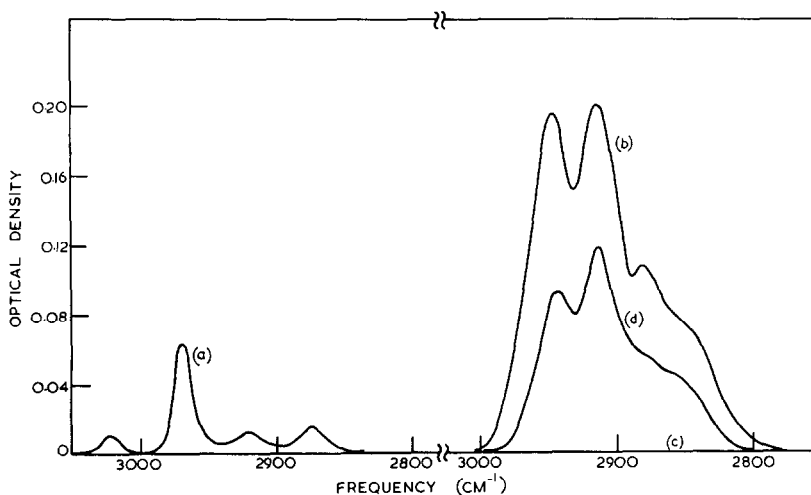

FIG. 4. Infrared spectra of 1-pentene on palladium at ~20°C after the following successive operations: (a) ~12-hr contact followed by 5-min pumping; (b) addition of hydrogen (50 Torr); (c) pumping; and (d) readdition of hydrogen (50 Torr).
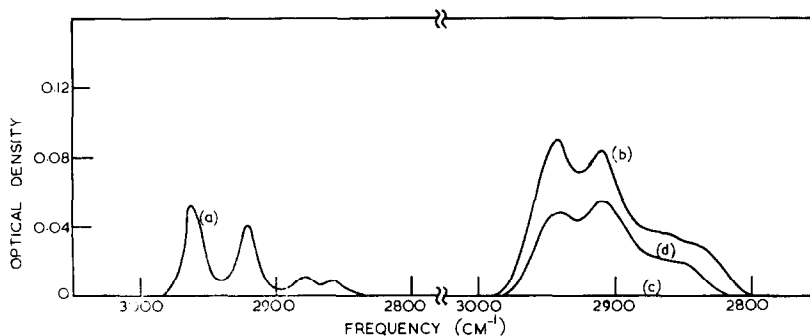
Fig. 5. Infrared spectra of propene (or cyclopropane) on palladium at ~20°C after the same successive operations described for 1-pentene (Fig. 4).

palladium pellet the strongly adsorbed species left after the second pump–hydrogenation cycle was less than half as intense as the corresponding species from 1-pentene suggesting that it was not quite as strongly adsorbed. In agreement with this, several pump–hydrogenation cycles tended to reduce the intensity of the spectra by a few percent each time.

Cyclopropane gave spectra identical in all respects to those from propene adsorption and indeed gas chromatographic analysis of the gas phase after the initial contact of cyclopropane indicated a significant concentration of propene in addition to propane, and excess cyclopropane.

The easily desorbed component from both propene and 1-pentene adsorption and hydrogenation may conceivably be either weakly chemisorbed or alternatively physically adsorbed alkane. Morrow and Sheppard (9) have identified a similar behavior following 1-butene adsorption and hydrogenation on nickel and platinum as being due to physically adsorbed n-butane which was in equilibrium with an easily detectable pressure of gaseous n-butane. However, the present experiment showed no evidence for gaseous alkanes. While this does not exclude the possibility of small amounts of physically adsorbed alkane contributing to the spectra, it is considered that the easily desorbed component is predominantly weakly chemisorbed. As a result of this, little can be gauged about the precise composition of this component. Instead, the attention of this paper will be directed towards the more clearly defined

and potentially more interesting, strongly adsorbed component left after the second pump–hydrogenation cycle.

The distinguishing features of the adsorbed species produced from this class of olefin were:

(i) weak but sharp bands after initial adsorption of the olefin.

(ii) Substantial intensification and frequency perturbation of the bands on the addition of hydrogen; and

(iii) a fraction of the species produced on initial hydrogenation was easily desorbed whereas the residual species were strongly chemisorbed and resisted desorption. These residual species were in rapid and reversible equilibrium with gaseous hydrogen such that evacuation of the gas phase completely dehydrogenated the adsorbed species to a carbonaceous residue.

Stepwise hydrogenation of the completely dehydrogenated residue showed that spectra intermediate between those of (c) and (d) in Figs. 4 and 5 were obtained always with the same ratio of optical densities of the 2945 to 2912 cm^{-1} bands as the respective fully hydrogenated species. The spectra obtained at saturation, viz, Figs. 4d and 5d remained unchanged at higher temperatures although somewhat higher pressures of hydrogen were required at the highest temperature studied, viz, 80°C. Furthermore, no new bands could be detected at any stage during dehydrogenation. In particular no circumstances could be found under which the spectra produced after initial adsorption of the olefin could

be regenerated. Thus while later hydrogenation and dehydrogenation was reversible the initial hydrogenation was not.

(c) The conjugated diolefin 1,3-butadiene. The spectra observed after contact of 1,3-butadiene with palladium, followed by pump–hydrogenation cycles are shown in Fig. 6. Band centers are again recorded in Table 1.

Distinguishing features of the adsorbed species were:

(i) no spectrum at all was observed after initial contact of the diolefin;

(ii) massive increase in intensity occurred on hydrogenation to produce bands with the same frequency as those from the adsorption of straight chain mono-olefins; and

(iii) slow dehydrogenation occurred on pumping such that rehydrogenation restored the original spectrum except that about 5 min was required for it to reach its full intensity. No desorption accompanied repeated pump–hydrogenation cycles.

Some difficulty was experienced in re-generating the pellet which had been exposed to 1,3-butadiene. For example, heating to 300°C in hydrogen for a few minutes failed to remove the last traces of adsorbed residues. The adsorbed residue was clearly more strongly adsorbed than 1-pentene which was easily desorbed by this treatment.

Nature of the Spectral Perturbations on Initial Hydrogenation

The irreversible perturbation of the more prominent v C–H bands to lower frequencies on initial hydrogenation has been shown to be greater for the linear olefins. This feature may be associated with the nature of the adsorbed species in the following way. Neglecting the weakly adsorbed component of linear mono-olefin adsorption and hydrogenation, the associated strongly adsorbed component is considerably more strongly adsorbed than the corresponding species derived from the branched chain olefins. As a result of this, it is supposed that the hydrogenated species derived from the linear mono-olefins are in more intimate
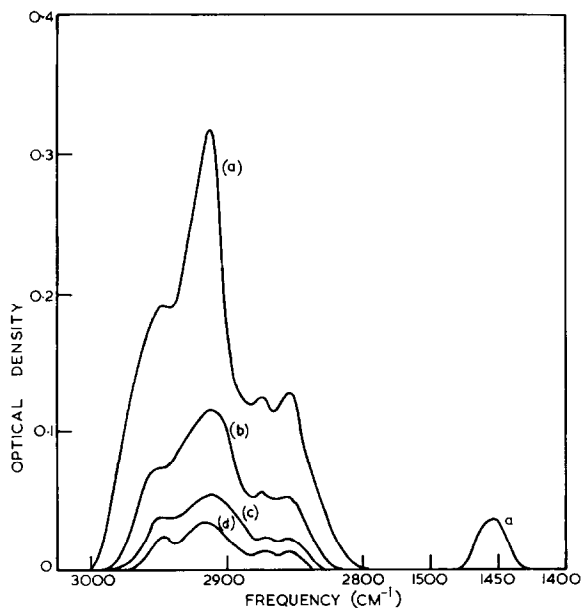

Fig. 6. Infrared spectra of 1,3-butadiene on palladium at ∼20°C after contact for ∼12 hr, pumping for 5 min, followed by: (a) addition of hydrogen (50 Torr) and pumping for (min): (b) 5; (c) 15; and (d) 30. Re-addition of hydrogen restored the spectra shown by (a). Note that initial evacuation of the gas phase produced no discernible spectrum.

contact with the surface and therefore more susceptible to pertubations by the surface. Before discussing the origin of the perturbation it is of interest to compare the magnitude of this effect with a more clearly defined case. For comparison the bands of n-pentane in the v C–H (asym) region are only slightly shifted from 2969 and 2939 cm^{-1} to 2964 and 2932 cm^{-1}, respectively, on dissolving the vapor in carbon tetrachloride. Thus the perturbation of the vCH$_3$ (asym) band seen with the linear mono-olefin ($\Delta v \sim 20$ cm^{-1}) is caused by an effect markedly greater than the normal van der Waals interaction of the condensed phase. The effect on the vCH$_2$ (asym) band is less pronounced ($\Delta v \sim 8$ cm^{-1}) and this is discussed below in connection with the structure of the adsorbed species.

Greater insight into the initial irreversible hydrogenation was gained by controlled dosing of hydrogen onto the surface species derived from 1-pentene adsorption,

when the spectral changes illustrated in Fig. 7 were observed. Even during the early stages of hydrogenation, when all the added hydrogen was sorbed by the system leaving a residual pressure of less than 10^{-3} Torr, broad bands at 2945 and 2912 cm^{-1} were beginning to appear at the expense of the sharp band at 2967 cm^{-1}. After addition of many hydrogen doses subsequent pumping and rehydrogenation produced the sequence of spectra normally observed.

The preparation of the sample prior to olefin adsorption must inevitably produce a monolayer of chemisorbed hydrogen. However, in excess olefin this is almost certainly stripped from the surface by hydrogenation of the olefin to form the corresponding alkane, leaving a hydrogen bare surface onto which further olefin may adsorb. Stephens (11) has shown that addition of hydrogen to a clean evaporated palladium film up to a residual pressure of 10^{-2} Torr results in the greater part of
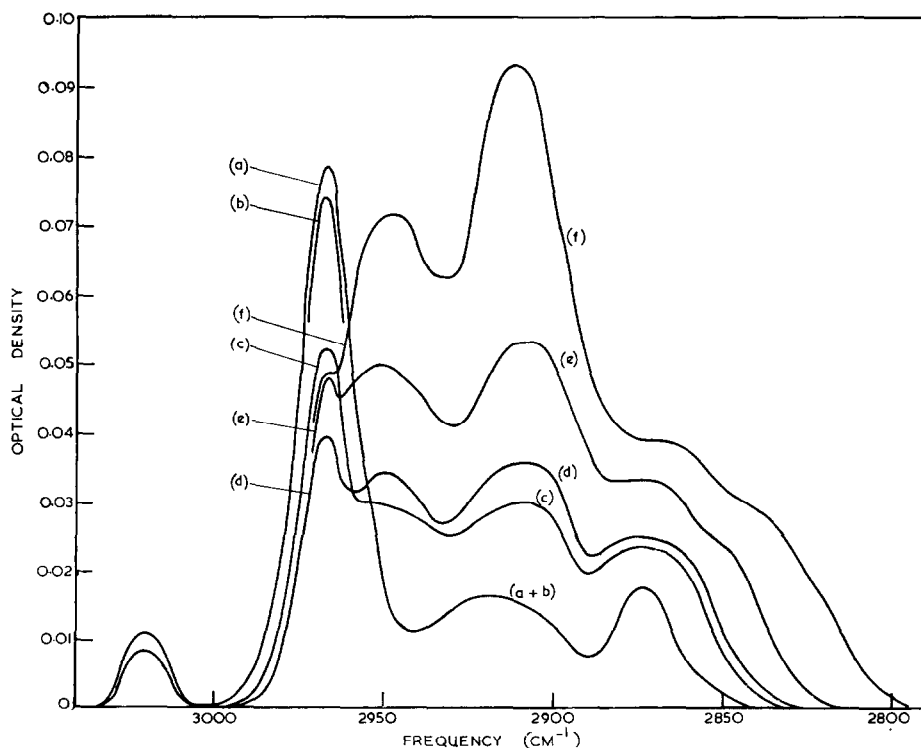

FIG. 7. Infrared spectra recorded during the controlled dosing of hydrogen onto the surface species derived from the adsorption of 1-pentene: (a) after $\sim$12-hr contact followed by evacuation for 5 min. and after successive doses of hydrogen up to a residual pressure of (Torr): (b) <10^{-3}; (c) <10^{-3}; (d) $\sim$2 × 10^{-3}; (e) 0.16; and (f) 0.55.

the hydrogen being adsorbed on the surface with only 3% entering the bulk of the metal as interstitially adsorbed hydrogen. About 50% of the adsorbed hydrogen was strongly adsorbed and could not be removed by pumping. The fate of the hydrogen dosed onto the hydrocarbon covered surface in the present experiment would have been twofold, viz, (i) dissociative adsorption onto the palladium surface with subsequent incorporation into the bulk; and (ii) hydrogenation of the adsorbed species. Thus at low residual pressures of hydrogen ($<10^{-2}$ Torr) which, in another paper (*12*) is shown to be too low for significant uptake by the chemisorbed residue, a monolayer of strongly and irreversibly chemisorbed hydrogen atoms would be formed on the sites left vacant between the adsorbed hydrocarbon residues by imperfect geometrical fitting. Thus after initial hydrogenation the vibrating C–H dipoles are subjected to an environment of Pd–H dipoles which may reasonably be expected to distort the normal C–H stretching vibrations. That chemisorption of hydrogen on palladium does indeed produce a polar bond can be inferred from the fact that hydrogen chemisorption on the transition metals is usually associated with a negative surface potential. The literature leaves this particular system undocumented presumably due to difficulties in interpretation due to the simultaneous absorption of hydrogen by bulk palladium.

The extent to which the dipole–dipole interactions may be expected to distort the C–H stretching vibrations will depend on the (i) magnitudes, (ii) separations, and (iii) relative orientations of the Pd–H and C–H dipoles. With the type of system of present interest, viz, a hydrocarbon chain with some flexibility chemisorbed on a geometrically heterogeneous substrate, all three of these factors are likely to be quite variable. The likely result is that there is a distribution of dipole–dipole interaction energies such that initial hydrogenation not only perturbs the bands to lower frequencies but also considerably broadens them. The breadth of the bands after hydrogenation can be contrasted with the equivalent bands of *n*-pentane condensed

in carbon tetrachloride. Here the relatively minor perturbations induced by van der Waals interactions of C–H dipoles when *n*-pentane vapor is condensed ($\Delta \nu \sim 5$ cm^{-1}) produces ν C–H bands which are still sufficiently sharp to separate the asymmetrical and symmetrical modes with an intermediate valley. On the other hand, the greater perturbing effect of the Pd–H dipoles on the adsorbed linear hydrocarbon also produces a wider spectrum of dipole–dipole interaction energies such that broader bands with no equivalent valley are observed (Figs. 4d and 5d).

Returning to the correlation between spectral perturbation and strength of adsorption the effect of chemisorbed hydrogen becomes more apparent. Thus the species derived from the linear olefins, which are strongly adsorbed and considered to be in intimate contact with the surface are subject to relatively large perturbations of the stretching vibrations ($\Delta \nu \sim 20$ cm^{-1}) by the surrounding carpet of Pd–H dipoles. On the other hand, the corresponding species derived from the branched chain olefins are in less intimate contact with the surface with the result that their C–H stretching frequencies are distorted correspondingly less ($\Delta \nu \sim 5$ cm^{-1}).

Initial hydrogenation of the species derived from adsorption of propene and 1-pentene (*10*) and 1-butene (*9*) on platinum and nickel results in equivalent perturbations typically about 5 cm^{-1}. This is considerably less than the equivalent linear species on palladium and could be due to either (i) the lower strength of adsorption of these olefins on platinum and nickel, or (ii) a lower M–H dipole moment on these two metals. While (ii) is purely speculative there is direct experimental evidence for (i) (*10*).

General Discussion

Spectral Assignments and Structure Determination

This aspect of infrared studies of hydrocarbons adsorbed on metal surfaces has always proved difficult because of
(a) doubts about the specific effect of

the metal surface on the absorption spectra of the adsorbed species;

(b) the various possibilities of the degree of dissociation of the adsorbed species at its point of contact with the surface; and

(c) the almost certain presence of a variety of structurally different adsorbed species.
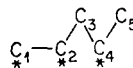
The approach adopted in the present work of comparing and contrasting the behavior of the spectra of the adsorbed species with the chemical and geometrical structure of the particular olefin is capable of leading to a greater insight into the nature of the adsorbed species without reference to detailed spectral assignments. In this way a firmer foundation has been layed for the interpretation of the finer points of the spectra.

Infrared bands of the adsorbed species in the ν C–H region occur almost exclusively in the saturated hydrocarbon region (below 3000 cm^{-1}). The single exception to this observed in the present work, viz, when initial adsorption of 1-pentene produced a relatively weak band at 3020 cm^{-1} will be discussed more fully below. Bands in the ranges 2945–2967 cm^{-1} and 2910–2920 cm^{-1} can be assigned to the asymmetric stretching modes of methyl and methylene groups, respectively. Bands assignable to the associated symmetric stretching modes occur in the region 2850–2880 cm^{-1} but are considerably weaker and often reduced to little more than shoulders on the relatively more intense bands of the asymmetric modes. The single band of a methine group of a hydrocarbon would be expected to occur at $\sim$2900 cm^{-1}. Bands in the δ C–H region ($\sim$1470 cm^{-1}) were occasionally sufficiently intense to be observed but were frequently incomplete due to the limited frequency range imposed on the system by the silica support (useful only down to $\sim$1400 cm^{-1}).

All the infrared bands seen in the present work can be adequately identified with those exhibited by simple hydrocarbons. This contrasts with previous infrared studies of adsorbed hydrocarbons where additional bands have been positively identified. The best example of this is the

chemisorption of ethylene on nickel, palladium, and platinum where a sharp well-defined band at $\sim$2880 cm^{-1} can be fairly convincingly assigned to associatively adsorbed ethylene MCH$_2$ CH$_2$ M (3, 6, 13). In addition each exhibited an associated weak band at $\sim$2790 cm^{-1} while on platinum and palladium a third broad band centered at 2930 cm^{-1} can also be assigned to this species (13). Ethylene adsorption in platinum and nickel both exhibited further additional bands which have been associated with the more highly dehydrogenated species (6). Similarly, 1-butene adsorption on platinum and nickel have revealed additional bands at 2870 cm^{-1}. Following the assignment of a similar band for adsorbed ethylene this band was assigned to a –CH$_2$* group of associatively adsorbed 1-butene (9).

In the absence of any equivalent bands in the present work it is concluded that the conspicuous features of the spectra are due to those parts of the adsorbed species not in direct contact with the surface. Thus in the hypothetical species, represented here without its constituent hydrogen
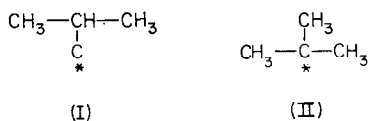
$$\overset{\displaystyle C_1}{\underset{*}{C_1}}-\overset{\displaystyle C_2}{\underset{*}{C_2}}\overset{\displaystyle C_3}{\diagup}\overset{\displaystyle C_5}{\diagup}\atop{\underset{*}{C_4}}$$

C$_1$, C$_2$, and C$_4$ will be referred to as absorbed carbon atoms while C$_3$ and C$_5$ are *free* alkyl groups and alone contribute to the conspicuous feature of the spectra. If the *adsorbed* carbon atoms are at all hydrogenated, it is inferred that their infrared spectra are either so weak, due to a low hydrogen content, or so broad that they are lost under the more clearly defined spectra of the *free* alkyl groups. For convenience adsorbed carbon atoms will be depicted as containing no hydrogen atoms. The significance of the asterisk is merely to indicate the point of attachment of the adsorbed species with the surface and in no way is intended to indicate the hydrogen content of the *adsorbed* carbon atoms.

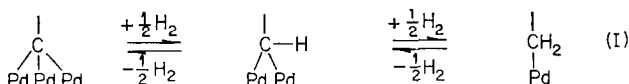*Structure of Adsorbed Branched Chain Mono-olefins*

Adsorption of isobutene produced species resulting in infrared bands assignable to

methyl and methine groups such that a mixture of species I and II may be considered to occur. Species II, if indeed it is formed at all, requires the acquisition

$$CH_3 \text{—} CH \text{—} CH_3 \qquad\qquad CH_3$$
$$\underset{*}{\overset{|}{C}} \qquad\qquad CH_3 \text{—} \underset{*}{\overset{|}{C}} \text{—} CH_3$$

$$\text{(I)} \qquad\qquad\qquad \text{(II)}$$

of an atom of hydrogen for each isobutene molecule adsorbed. This conceivably could arise from the monolayer of hydrogen which covers the palladium surface prior to olefin adsorption. The existence of an inherently weaker methine band near 2910 cm^{-1} shows that (I) must make at least a nontrivial contribution to the adsorbed species. The previous conclusion that the adsorbed species are not strongly adsorbed and therefore not in intimate contact with the surface argues against the existence of more multiply bonded species and furthermore appears to favor the existence of species like (I) where the methyl groups are well removed from the surface.

The comparatively small increase in intensity ($\sim 50\%$) of the spectrum or initial hydrogenation can be attributed to a partial hydrogenation of the adsorbed carbon atom in species (I) according to Eq. I:

of a band at 3020 cm^{-1} due to olefinic carbon atoms; and (ii) the almost complete absence of methylene groups.

This system produced the only example in the present study of a band above 3000 cm^{-1} (at 3020 cm^{-1}) conventionally assignable to an olefinic carbon atom of the type

$$=C\overset{H}{\underset{R}{\diagup}} \cdot \text{ No comparison band at 3080 cm}^{-1} \text{ due to a } =C\overset{H}{\underset{H}{\diagup}}$$
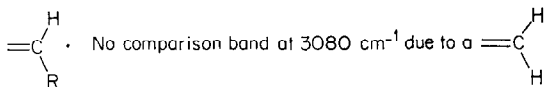
group was ever detected. The species responsible for the 3020 cm^{-1} band is probably better represented by

$$R \text{—} \underset{*}{CH} = CH \text{—} \underset{*}{R'}$$

$$\text{(III)}$$
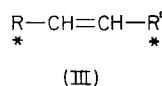
rather than the dissociatively adsorbed olefin, e.g.,

$$\underset{\underset{*}{Pd}}{\overset{CH=C\text{—}R}{\diagup}}\underset{\underset{*}{Pd}}{\diagdown}$$

$$\text{IV}$$
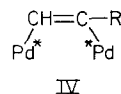
for the following reasons:

(a) It is shown below that although 1-pentene was used, double bond isomerization intervenes to produce a surface species based on 2-pentene which has no olefinic

$$\underset{Pd\,Pd\,Pd}{\overset{\overset{|}{C}}{\diagup\overset{|}{}\diagdown}} \quad \underset{-\frac{1}{2}H_2}{\overset{+\frac{1}{2}H_2}{\rightleftharpoons}} \quad \underset{Pd\,Pd}{\overset{\overset{|}{C}\text{—}H}{\diagup\diagdown}}$$

$$\underset{-\frac{1}{2}H_2}{\overset{+\frac{1}{2}H_2}{\rightleftharpoons}} \quad \underset{Pd}{\overset{\overset{|}{CH_2}}{\overset{|}{}}} \quad \text{(I)}$$

The hydrogen bearing *adsorbed* carbon atom so formed is then considered to have an ill-defined spectrum which merely contributes to the overall intensity (particularly in the 2920 cm^{-1} region) without producing new bands. An equilibrium of the type shown in Eq. (I) can also be used to explain the intensity increase when the adsorbed residue produced by initial hydrogenation followed by evacuation (Fig. 2d) is rehydrogenated (Fig. 2e).

Structure of Adsorbed Linear Mono-olefins

The spectrum of initially adsorbed 1-pentene contained two features which require attention. These are (i) the presence

hydrogen atoms when bonded as a dissociatively adsorbed olefin, and

(b) If dissociatively adsorbed olefins like species IV were produced it would be difficult to account for the absence of a band near 3020 cm^{-1} from propene adsorption. Thus with olefins containing an alkyl chain, the extent to which this part of the molecule may provide some of the impetus for chemisorption, while leaving the olefinic double bond intact, must also be considered. In this way species like III may be formed. Clearly a longer alkyl chain in species III will lead to stronger adsorption and therefore a better chance of the double bond being unaffected by adsorption. As a result

of this, the initial mode of propene adsorption appears to be confined to the olefinic double bond without there being any evidence for species produced by adsorption solely through the single methyl group. On the other hand, 1-pentene, with three alkyl carbon atoms can apparently form species like III of sufficient stability.

The almost complete absence of methylene groups in the spectrum of adsorbed 1-pentene can be attributed to double bond isomerization of the parent 1-pentene to cis- and trans-2-pentene. At 25°C the equilibrium lies heavily in favor of the 2-pentenes (>98%) so that surface species based primarily on adsorption of these isomers would be preferred. Indeed, gas chromatographic analysis, after contact of excess 1-pentene (15 Torr) with the pellet, revealed the presence of new products in the relative proportions n-pentane (5%), trans-2-pentene (55%), and cis-2-pentene (45%) while unreacted 1-pentene represented 90% of the gas phase. Although the reaction was clearly poisoned by adsorbed species before gaseous equilibrium was established, complete equilibrium of the adsorbed phase may be anticipated such that species of the type

$$\underset{*}{\overset{CH_3}{\diagdown}}\underset{*}{\overset{CH_2-CH_3}{\diagup}}$$
$$C-C$$

$$V$$
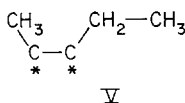
which are relatively richer in *free* methyl groups may reasonably be expected as the dominant initial product of adsorption. However, in order to account for the large increase in absorption intensity on initial hydrogenation, and the almost complete absence of methylene groups, self-hydrogenation must also occur to produce more highly dehydrogenated residues, most probably of the type

$$\underset{*}{C}-\underset{*}{C}-\underset{*}{C}-\underset{*}{C}\overset{CH_3}{\diagup}$$
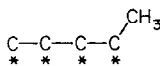
and perhaps even a completely dehydrogenated C_5 surface carbide. Eischens and Pliskin (2) have similarly shown that as a result of double bond isomerization, the

isomeric hexenes adsorb on nickel to give the same surface species.

Initial adsorption of propene (or cyclopropane) produced comparable intensities of the infrared bands due to methyl and methylene groups. However, as hydrogenation of this system also produced a large increase in absorption intensity this spectrum is unlikely to be due to

$$^{*}C-CH_2-CH_3.$$
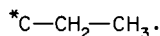
Instead, more extensive dissociation of the associatively adsorbed olefin probably occurs to produce surface species comparable to those formed during pentene adsorption. The species likely to be present are

$$\underset{*}{C}-\underset{*}{C}-\underset{*}{C}, \ \underset{*}{C}-\underset{*}{C}-CH_3, \text{ and } \ \underset{*}{C}-CH_2-\underset{*}{C}.$$
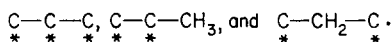
It is difficult to account for the presence of a methylene group in the spectrum when comparable species from 1-pentene adsorption appears to be almost completely absent.

Addition of hydrogen to the species produced either from propene or pentene adsorption leads to a perturbation of the stretching frequencies of the *free* alkyl groups and as the hydrogen pressure increases, to an incorporation of hydrogen into the adsorbed residue. The model discussed earlier to explain the irreversible perturbation of the stretching frequencies on initial hydrogenation requires that all the *free* alkyl groups of the adsorbed species be in intimate contact with the surface. It is therefore considered improbable that hydrogenation of the species produced by adsorption of linear mono-olefins is so extensive that, for example, an n-alkyl species results. Instead, the proposed model is one in which the fully hydrogenated species is still bound to the surface at many points such that the *free* alkyl groups are adjacent to a *bonded* carbon atom. Within this criterion a number of structurally different adsorbed species may be envisaged. A selection of the species considered likely to be present are shown in Fig. 8c for the hydrogenation of adsorbed pentene. It remains to comment on the different per-
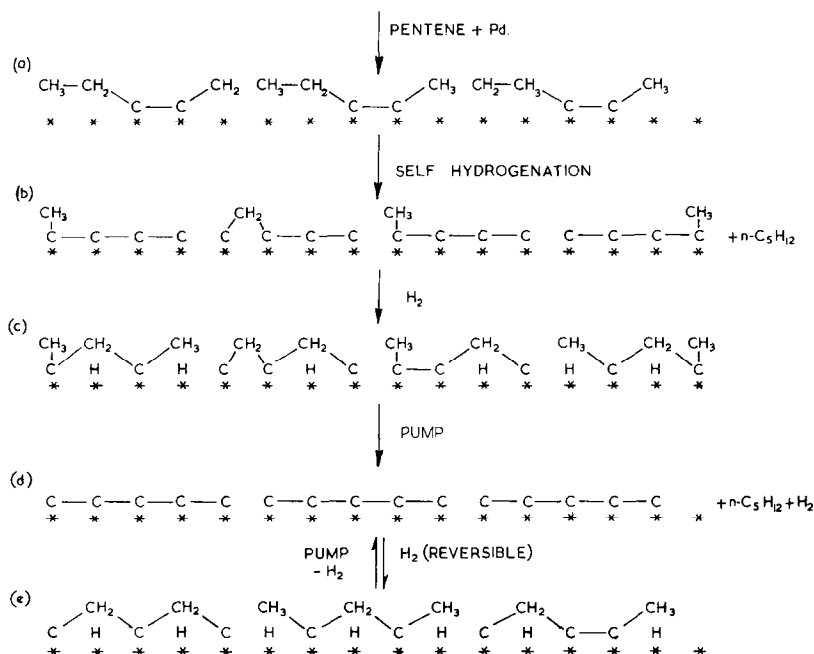
FIG. 8. Proposed model for the adsorption of 1-pentene on palladium followed by hydrogenation–evacuation cycles. For simplicity, adsorbed species containing olefinic groups (species III) have been neglected. The asterisks indicate an array of surface palladium sites and again are not intended to indicate the hydrogen content of the *adsorbed* carbon atoms except that dehydrogenation by evacuation (d) does lead to a residue containing no detectable hydrogen.

turbations experienced by the methyl and methylene νC–H (asym) bands following adsorption and hydrogenation of, for example, 1-pentene. Comparison of the bands of the adsorbed species with the corresponding gas phase molecule (n-pentane) shows that adsorption led to a greater perturbation of the methylene band ($\Delta\nu \sim$ 19 cm^{-1}) than the methyl band ($\Delta\nu \sim 1$ cm^{-1}). On the other hand, hydrogenation of the adsorbed species resulted in a greater perturbation of the methyl band ($\Delta\nu \sim 23$ cm^{-1}) than the methylene band ($\Delta\nu \sim 8$ cm^{-1}). The proposal that the adsorbed species are in intimate contact with the surface demands that the methylene groups are in a somewhat strained bridged configuration,

$$\begin{array}{c} CH_2 \\ C \quad C \\ * \quad * \end{array},$$

whereas the methyl groups,
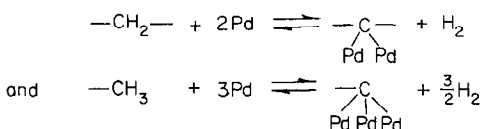
$$-\underset{*}{C}-CH_3,$$
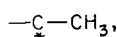
still possess much the same freedom as in a gas phase molecule. Consequently, it is to be expected that adsorption will have a greater effect on the stretching vibration of the methylene groups. Similarly, the dipolar perturbation which is believed to occur on initial hydrogenation may also be influenced by this kind of geometrical effect. As a result of this, the stretching vibration of methyl groups should be the more representative of the effects due solely to dipolar interactions.

After desorption of the weakly absorbed component and when the hydrogen is evacuated from the cell in a stepwise manner the infrared spectrum of the strongly chemisorbed species decreases uniformly in intensity without any alteration in the ratio of *free* methyl to *free* methylene groups. Thus these groups become *bonded* carbon atoms without any bias towards the preferential adsorption of one group over the other. Furthermore, dehydrogenation occurred without the appearance of

any new bands. Thus dehydrogenation occurred without any change in the hybridization of the carbon atoms and a mechanism like

$$-CH_2-\ \rightleftharpoons\ =C\overset{H}{\underset{\diagdown}{\diagup}}\ +\tfrac{1}{2}H_2$$
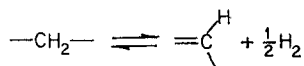
must be rejected. Instead, the carbon atoms remain saturated in which case the palladium substrate must form a Pd–C σ-bond for every hydrogen atom removed from the adsorbed residue. As a result of this, stoichiometric equilibrium of the type

$$-CH_2-\ +\ 2Pd\ \rightleftharpoons\ \underset{Pd\ \ Pd}{-C-}\ +\ H_2$$

$$\text{and}\qquad -CH_3\ +\ 3Pd\ \rightleftharpoons\ \underset{Pd\ Pd\ Pd}{-C\diagdown}\ +\tfrac{3}{2}H_2$$

can be written to describe the overall dehydrogenation–hydrogenation equilibria. If the spectra of the fully hydrogenated species (Figs. 4d and 5d) contained unresolved bands due to groups like

$$\underset{Pd\ Pd}{-C\overset{\diagup}{H}\diagdown}\ ,\ \underset{Pd}{-CH_2,}\ \text{or}\ \underset{Pd}{-CH-}\ ,$$
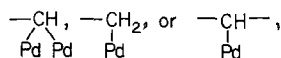
equivalent equations could also be written to describe their equilibria with gaseous hydrogen. In the limit, when all the hydrogen is evacuated from the cell, a carbonaceous residue must remain on the surface. The reaction is perfectly reversible and rehydrogenation restores the original spectrum of the strongly chemisorbed species. A fuller thermodynamic and kinetic study of this reaction will be reported elsewhere (12).

Preliminary studies of the hydrogenation and dehydrogenation of the corresponding adsorbed species on platinum and nickel have indicated that the equilibrium is achieved much more slowly compared to palladium (11). It is therefore tempting to relate this unique feature of palladium with its well-known ability to rapidly absorb interstitial hydrogen into its bulk. Thus interstitial hydrogen could bring about hydrogenation of the carbonaceous residue by approaching it from within the bulk of metal such that it breaks the Pd–C σ-bond with the simultaneous formation of a C–H σ-bond. In this case the proximity the hydrogen to the Pd–C bond in the activated complex is convenient for steric consideration (Fig. 9).

A possible model for the adsorption and hydrogenation of 1-pentene is shown in Fig. 8. It is not intended that the adsorbed species shown here are representative of all those possible but instead only indicates the type of reactions expected of a selection of the proposed adsorbed species. As pointed out above, it is expected that initial adsorption is accompanied by double bond isomerization to produce species based primarily on 2-pentene adsorption (Fig. 8a) with self-hydrogenation rapidly producing more highly dehydrogenated residues which contain very few methylene groups (Fig. 8b). The extent to which these adsorbed species may dehydrogenate is probably dictated by a competition for the available sites by the *free* alkyl groups of the initially adsorbed species (Fig. 8a)
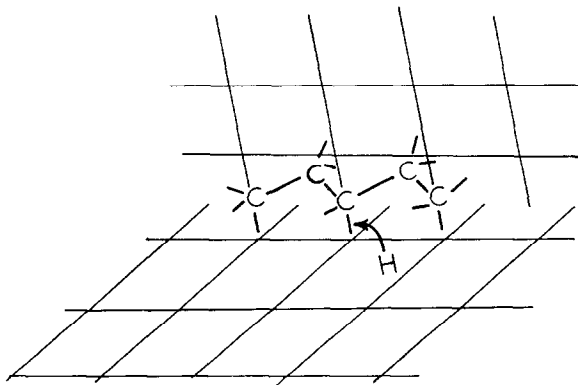

FIG. 9. Proposed model for the adsorption of a dehydrogenated C₅ residue at a step or ridge site on the palladium surface.

and the olefinic double bond of a gas phase molecule. This competition provided by the excess olefin in the gas phase limits the complete dehydrogenation of the adsorbed species such that there is still the occasional CH_3 group, and to a less extent CH_2 group, forced above the chemisorbed layer to contribute to the absorption spectrum. Under these conditions the surface is believed to be oversaturated with carbon atoms. Addition of hydrogen, while hydrogenating some of the *adsorbed* carbon atoms will aggravate this situation due to the additional competition for the available site provided by the chemisorption of hydrogen (Fig. 8c). On subsequent pumping, it is not surprising that a fraction of the adsorbed species are desorbed leaving just enough to be accommodated by the available sites (Fig. 8d). Thus this model does not distinguish between the apparently weakly and strongly chemisorbed species but instead considers the observed structural changes as being due to a decrease in the competition for the available sites as a component of the chemisorbed residues is desorbed and pumped away, most probably as *n*-pentane. In this way it is understandable why the ratio of *free* methyl to methylene groups decreases as this component is desorbed for the following reasons. The competition between the adsorbed residues for the limited number of sites will be most keenly felt at the ends of the carbon chains where it is sterically easier to force a methyl group above the plane of *adsorbed* carbon atoms. Furthermore, it will be proposed later that adsorption occurs at ridge and step sites on the surface where the available sites will approximate a linear array. In this way the *adsorbed* nonterminal carbon atoms (i.e., those leading to methylene groups on hydrogenation) are protected from competition for the available sites by adjacent adsorbed species.

Structure of Adsorbed 1,3-Butadiene

The lack of a spectrum from initial adsorption of 1,3-butadiene can also be understood by reference to Fig. 8. In this case no alkyl function is available in the adsorbed molecule to be displaced above

the adsorbed layer by preferential adsorption of gaseous olefin. The resulting species is almost certainly a multiply bonded carbonaceous residue in which case the surface is not oversaturated with adsorbed species. Therefore, unlike the linear mono-olefins, hydrogenation did not lead to a weakly adsorbed component. Hydrogenation of this surface species produced a very intense spectrum compared with the other linear olefins. The hydrogenated species was considerably richer in methylene compared with methyl groups. This suggests that polymerization had occurred to form a strongly adsorbed linear C_{4n} species. It is probable that in this case, the surface is effectively saturated with these species such that adsorption of hydrogen on the residual sites is greatly inhibited. It has already been considered that the hydrogenation and dehydrogenation of the adsorbed hydrocarbon occurs with interstitially absorbed hydrogen which is in equilibrium with the gas phase via chemisorbed hydrogen. In this way it is understandable how the rate of equilibration of gaseous hydrogen and the hydrogen of the adsorbed species could be inhibited to the extent that time dependent spectra were observed on pumping and rehydrogenation. With this exception the species derived from the adsorption and hydrogenation of 1,3-butadiene resembles the general behavior of the strongly adsorbed component from the adsorption and hydrogenation of the linear mono-olefins.

Strength of Adsorption of the Adsorbed Species

From the uptake of hydrogen by the initially adsorbed species the degree of dehydrogenation of these species (i.e., extent of dissociative adsorption) can be written in the following order: 1,3-butadiene > linear mono-olefin > branched chain mono-olefins. However, in no case could any of these species be desorbed by evacuation at 20°C. The order of the strength of adsorption of the hydrogenated species can similarly be written thus: 1,3-butadiene > 1-pentene > propene = cyclopropane > iso-butene > 4,4-dimethyl-1-pentene. This, of course, neglects the easily desorbed com-

ponent produced on initial hydrogenation of the linear mono-olefins, which appear to be even less strongly adsorbed than the corresponding species produced from the branched chain mono-olefins.

This latter order is similar to the one expressed above for the degree of dehydrogenation of the adsorbed species after adsorption of the olefin. Clearly the more highly dehydrogenated species have greater contact with the surface by the formation of multiple Pd–C bonds and are consequently more strongly adsorbed, even after hydrogenation.

It is of interest to note that with the straight chain mono-olefin the strength of adsorption increases with increasing molecular weight whereas the reverse was observed for the branched chain mono-olefins. Thus while the alkyl part of the linear mono-olefins participates in adsorption, the same does not appear to be the case with the branched chain mono-olefins. In the latter case it has already been concluded that bonding occurs solely through the olefinic bond with the alkyl part of the molecule remaining essentially inert to adsorption.

Geometrical Considerations

In the fully dehydrogenated residue resulting from linear mono-olefin adsorption a mode of adsorption must be sought whereby the 12 sp^3 orbitals of a C_5 residue for example, may be multiply bonded to an area of the palladium surface no greater than ~20 $Å^2$. Clearly the geometric constrains are too severe for this to be feasible on a low index plane like the (111) or (100), which are effectively planar on the atomic scale. Furthermore, some of the sp^3 orbitals must necessarily be oriented away from such a surface and therefore cannot interact with it. However, if the molecule is considered to adsorb at a step in the surface as shown in Fig. 9 all the sp^3 hybrid orbitals have a better opportunity to interact with the surface metal atom. There would appear to be no reason why the step could not be simply a ridge of no more than atomic dimensions on, for example, the (113) face. Computations

have shown that with the metal particle size distribution likely to be present when a metal is dispersed by Aerosil (viz, 20–70 Å) sites at crystallographic steps or ridges are to be expected and may represent up to 25% of the surface (14). In view of the special arrangement of sites believed to be necessary for the extensive multiple adsorption of the strongly adsorbed species, the corresponding weakly adsorbed fraction could, as an alternative to the model discussed earlier, be considered to adsorb on those areas of the palladium surface which are atomically smoother. The branched chain olefins appear to be nondiscriminatory about the sites on which they adsorb and require only a limited number of no special geometry for each molecule adsorbed. Their adsorption is consequently not confined to a particular area of the palladium surface. This characteristic of these olefins can be related to their additional complexity in geometry which prevents the adsorbed molecule from taking up a configuration to match that of the more active sites at a step or ridge in the surface.

On the Possibility of n-Alkyl Groups (following hydrogenation of the linear mono-olefins)

Previous infrared studies have invariably interpreted the spectra observed after adsorption and hydrogenation of olefins as being due to n-alkyl groups (1–3, 5–9). This interpretation was based purely on the spectroscopic grounds that the observed ratio of methyl to methylene groups was consistent with such a species. However, the present work on palladium has shown that while the species derived from the adsorption and hydrogenation of the branched chain mono-olefins was most probably an alkyl type of species, a similar interpretation for the straight chain olefins is unlikely for the following reasons.

(a) An n-alkyl species would be unable to account for the profound differences in the spectra observed from the linear and branched chain olefins. It was shown that following hydrogenation, the linear olefins are much more strongly adsorbed than the

branched chain olefins and must therefore be more extensively bonded to the surface. This characteristic was rationalized with the different spectral perturbation observed on initial hydrogenation of the two classes of olefin.

(b) During deuterium exchange with n-pentane and n-hexane over evaporated palladium films at 20–120°C (15, 16) triadsorbed species have been postulated from the resulting distribution of deuteroalkanes. In these cases, the adsorbed species are not so strongly adsorbed that equilibrium with the gas phase is prevented. Therefore, it is supposed that the species observed in the present work, which cannot be desorbed in the presence of hydrogen, must be more strongly adsorbed by virtue of their multiple contact with the surface as proposed in Fig. 8e.

(c) The unreliability of a purely spectroscopic interpretation is evident when the strongly adsorbed component from linear mono-olefin adsorption and hydrogenation is dehydrogenated in a stepwise manner. Under these conditions spectra with identical ratios of methyl and methylene groups were observed as the overall intensity decreased. Thus, although each of these spectra was consistent with an n-alkyl group corresponding to the appropriate olefin it is clear that the adsorbed species was becoming progressively more highly dehydrogenated until in the limit, when all the hydrogen had been evacuated, only a carbonaceous residue remained.

Comparison of the behavior of these olefins over palladium with other studies of 1-butene (9), propene, and 1-pentene (10) over platinum and nickel shows that the order of the strength of adsorption of the hydrogenated species on these three metals occurs thus

Pd > Ni > Pt.

Over platinum the hydrogenated species could be readily desorbed by evacuation at room temperature and in this respect resembled the corresponding species from isobutene adsorption on palladium. It is therefore considered likely that over platinum the hydrogenated species resembles an n-alkyl group which readily desorbs to give physically adsorbed n-butane as proposed by Morrow and Sheppard (9).

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