Reversible Uptake of Hydrogen by Hydrocarbons Chemisorbed on Palladium

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The reversible uptake of hydrogen by a hydrocarbon residue chemisorbed on silica-supported palladium was quantitatively studied by ir spectroscopy. Adsorption isotherms of hydrogen in the range 20–80°C showed $\theta \propto \sqrt{p}$ and yielded an isosteric heat of adsorption of 12.5 kcal mole^{-1} which was independent of coverage in the range studied, viz., $0.2 < \theta < 0.9$.

The exchange of the adsorbed hydrocarbon with deuterium and the reverse exchange with hydrogen at 40–80°C was shown to follow first-order kinetics. The activation energy was 18 kcal mole^{-1} and a kinetic isotope effect of $\sim$3 increased the rate of hydrocarbon exchange compared with deuterocarbon exchange. The thermodynamic and kinetic studies were related and a potential energy diagram was constructed to describe the energetics of adsorption of hydrogen.

INTRODUCTION

From the earliest ir studies of olefins adsorbed on metal surfaces, it was recognized that hydrogenation of an adsorbed olefin led to adsorbed species, which could be successively hydrogenated and dehydrogenated by the mere addition and evacuation of hydrogen (1–6). The experimental manifestation of this effect was the partial disappearance of the ir bands in the ν_{C-H} region when the hydrogen gas phase was evacuated. These ir bands could be almost completely restored by the readdition of hydrogen, thereby showing that the phenomenon did not involve an equilibrium with gaseous hydrocarbon, but instead represented the reversible making and breaking of C–H bonds in the adsorbed species.† Much of this earlier work was carried out with nickel and, to a lesser extent, platinum as the adsorbent. In these cases, the equilibrium was not clearly defined since

evacuation of hydrogen never completely dehydrogenated the adsorbed species, and furthermore some desorption invariably occurred. More recently it was shown that the same species produced by the adsorption and hydrogenation of linear mono-olefins (in particular 1-pentene) on palladium produced the most rapid and reversible example of this effect yet reported (7).

The interpretation given in this work (7) to the processes of adsorption and hydrogenation of these olefins can be summarized as follows. Adsorption of the linear mono-olefins on palladium produced a highly dehydrogenated residue, which upon initial hydrogenation yielded a weakly and a strongly adsorbed component. The weakly adsorbed component was easily removed at room temperature by brief evacuation followed by rehydrogenation. It is the residual strongly adsorbed component which is the sole concern of this paper, and future references to the adsorbed species will refer to this component unless it is otherwise specified.

From a comparison of the characteristics of the adsorption and hydrogenation of linear and branched chain olefins on palladium, it was concluded that the linear ole-

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† To distinguish this hydrogen from that sorbed by the metal, it will henceforth be referred to as skeletal hydrogen.

fins produced adsorbed species which were in intimate contact with the surface. The constituent carbon atoms could be classified as either *adsorbed* carbon atoms or *free* alkyl groups.* A *free* alkyl group refers to a carbon atom which is not bonded to the surface and in a linear species must be either a methylene,

$$C-CH_2-C,$$
$$* \qquad *$$

or a methyl,

$$C-CH_3,$$
$$*$$
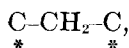
group. It was proposed that these groups produced the only discernible ir absorption maxima in the spectrum; at 2912 cm^{-1} (ν-CH$_2$ asym) and 2945 cm^{-1} (ν-CH$_3$ asym). Weaker bands at 2880 cm^{-1} and 2860 cm^{-1} due to the corresponding symmetric modes were imperfectly resolved. The associated *adsorbed* carbon atoms designated $-C-$ and $-C$ are written with
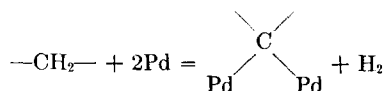   *   *
asterisks to indicate their attachment to the surface, and in no way is intended to suggest the hydrogen content of these atoms. In the absence of any ν_{C-H} absorption maxima which could be assigned to species other than the *free* alkyl groups, it was concluded that if the *adsorbed* carbon atoms also contained C–H bonds, then their characteristic ir absorption was so ill defined that it could not be resolved above the more clearly defined spectrum of the *free* alkyl groups. The strength of the adsorption of these species prompted the suggestion that the adsorbed species was extensively bonded to the surface and of the type

$$\begin{array}{ccc} & CH_2 & CH_3 \\ & \diagup \quad \diagdown \diagup \\ C-C & & C \\ * \quad * & & * \end{array}$$
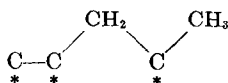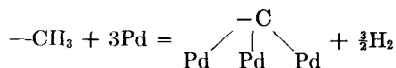
Comparable species within the general theme that *free* alkyl groups are adjacent to *adsorbed* carbon atoms are also possible, and indeed it appears likely that the adsorbed layer consists of a variety of structurally different species.

* Reference to *bonded* carbon atoms in (7) is inconsistent and in these instances should read *adsorbed* carbon atoms.

The dehydrogenation of the adsorbed species by stepwise evacuation of hydrogen occurred without any bias towards the preferential dehydrogenation of one group over another. That is to say, the ir spectrum in the ν_{C-H} region decreased uniformly in intensity without any alteration in the ratio of the optical densities of the 2945 cm^{-1} and 2912 cm^{-1} bands. Furthermore, dehydrogenation occurred without the appearance of any new bands which shows that the hydrogen bearing carbon atoms retained their sp^3 hybridization. As a result of this, the hydrogenation–dehydrogenation equilibrium must occur by the reversible making and breaking of C–H and C–Pd σ-bonds according to the following stoichiometric equilibria:

$$-CH_2- + 2Pd = \begin{array}{c} \diagdown C \diagup \\ \diagup \quad \diagdown \\ Pd \qquad Pd \end{array} + H_2$$

and

$$-CH_3 + 3Pd = \begin{array}{c} -C \\ \diagup \ | \ \diagdown \\ Pd \ \ Pd \ \ Pd \end{array} + \tfrac{3}{2}H_2$$

It is these equilibria which are the sole concern of this paper. By using the ir spectrometer merely to monitor the hydrogen content of the adsorbed species the form of the adsorption isotherm and the isosteric heat of adsorption were determined. In a second experiment, the rate at which this process was established in excess hydrogen (or deuterium) was studied kinetically by isotope exchange.

EXPERIMENTAL

The experimental apparatus and procedure for preparing the adsorbed species has been described previously (7). Basically, a conventional silica-supported palladium pressed pellet was mounted in an ir cell which permitted rapid thermal transfer to a Dewar, which was incorporated into the cell. This feature of the cell allowed any temperature in the range —100–300°C to be rapidly attained, and then conveniently maintained by either altering the heating current or adding a little liquid nitrogen to the Dewar. With experience this arrangement allowed temperatures in the range

0–100°C to be controlled to within ±1°C.

Adsorption and hydrogenation of linear mono-olefins on palladium has been shown to lead to both weakly and strongly adsorbed components (7). As only this latter component is of interest to the present study the sample was subjected to several pump-hydrogenation cycles before making quantitative measurements. Although only a single cycle was necessary to remove the weakly adsorbed component, it was found that many cycles assisted in flushing the residual olefin from the stopcock grease. This olefin would otherwise desorb and hydrogenate to give physically adsorbed alkane, thereby interfering with subsequent quantitative measurements. The spectrometer was placed adjacent to the vacuum line so that the cell could be connected to it by about a three foot length of glass tubing fitted with ball and socket joints. Thus, gas manipulation could be achieved without removing the cell from the spectrometer. For quantitative measurements, it was essential for the same section of the pellet to be traversed by the ir beam during a series of measurements. Since the temperature range of interest, viz., 20–80°C, was not greatly different from the natural equilibrium temperature of the system while exposed to the ir beam (~40°C), it was believed that the temperature as recorded by the thermocouple was essentially identical to the equilibrium temperature of the pellet. Thermal equilibration was assisted by the characteristic that skeletal adsorption only occurred with a significant pressure of hydrogen (0.1–100 Torr), which increased with temperature. Hydrogen and deuterium pressures were measured from one of two tilting McLeod gauges, which jointly covered the range 0.001–10 Torr, while pressures in excess of this were measured directly from a mercury manometer.

This study was primarily concerned with measuring the concentration of C–H (or C–D) bonds in the adsorbed species. Therefore, the spectrometer was used merely to measure this concentration by equating it to the optical density of a particular band in the spectrum. Thus, C–H and C–D concentrations were monitored from the optical density of the ν_{C-H} and ν_{C-D} bands at 2912 cm^{-1} and 2185 cm^{-1}, respectively. Specific concentrations could not be determined in this study since neither the surface concentration nor the extinction coefficient of the adsorbed species were known. However, this did not prove to be a severe limitation. The justification for selecting a particular ir band to monitor the overall concentration of hydrogen (or deuterium) in the adsorbed species is due to the observation that the methyl and methylene groups are dehydrogenated and exchanged without any bias towards the preferential reaction of one group over the other.

RESULTS AND INTERPRETATIONS

Adsorption Isotherms and Isosteric Heat of Adsorption

Adsorption and desorption isotherms were determined by recording the spectrum in the ν_{C-H} region as a function of increasing and decreasing hydrogen pressure, respectively. Typical spectra for the adsorption of hydrogen at 50°C on to the absorbed species derived from 1-pentene adsorption are shown in Fig. 1. The uptake of hydrogen by the adsorbed species was expressed as a fractional saturation defined thus,

fractional saturation, θ

$$= \frac{\text{optical density at } p,T}{\text{optical density at saturation}}.$$

The optical density at saturation for each isotherm was obtained by admitting a large dose of hydrogen (60–200 Torr, increasing with temperature from 20 to 80°C), to the cell. At each temperature studied, increasing the hydrogen pressure still further had no detectable effect on the spectra showing that the choice of unit saturation had a realistic significance. The resulting isotherms at 10°C intervals in the range of 20–80°C are shown in Fig. 2. For clarity, the experimental points are shown only for the 20, 50, and 80°C isotherms. Before commencing at a new temperature, the sample was pumped for about 30 sec before admitting hydrogen to the cell.
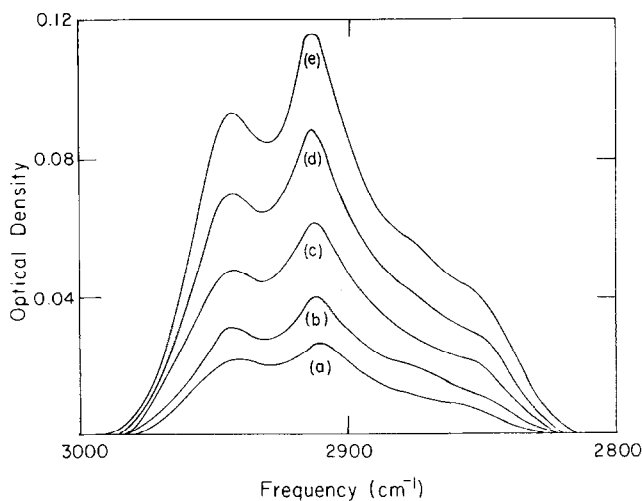
FIG. 1. Infrared spectra obtained during the controlled dosing of hydrogen at 50°C to the adsorbed species derived from 1-pentene. Pressure of hydrogen: (a), 0.16 Torr; (b), 0.33 Torr; (c), 1.1 Torr; (d), 3.2 Torr; (e), 60 Torr.

The optical density at saturation of the adsorbed species derived from 1-pentene was unchanged by the adsorption temperature. Furthermore, numerous pump-hydrogenation cycles did not lead to any desorption of the adsorbed species as judged by the optical density at saturation. However, the corresponding species from propene or cyclopropane adsorption could be desorbed by the same repetitive procedure (7). Thus, while the optical density at saturation of the adsorbed species decreased by up to

20% during a series of pump-hydrogenation cycles, no effect on the isotherms could be detected when each new isotherm was normalized to the appropriate optical density at saturation. As with the adsorbed species derived from 1-pentene, the optical density at saturation of the corresponding species from propene and cyclopropane adsorption was unchanged by temperature. Thus, each of the three adsorbed species could be saturated at any temperature in the range 20–80°C by the addition of
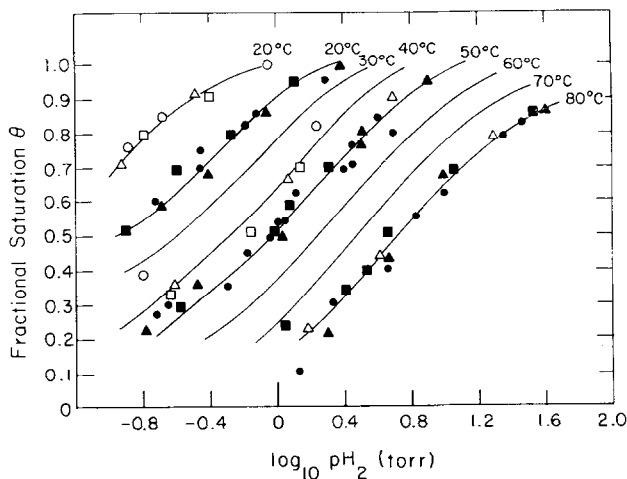

FIG. 2. Isotherms for the skeletal adsorption of hydrogen by the adsorbed residue derived from: cyclopropane, ●; propene, ■ and 1-pentene, ▲. The desorption isotherms are indicated by the corresponding open symbols. For clarity, experimental points are only indicated for the 20, 50, and 80°C isotherms.

sufficient hydrogen. As a result of this, iso-steres can be interpolated directly from Fig. 2.

Both adsorption and desorption isotherms were measured, and, with the usual equilibration times allowed (~4 min), hysteresis was observed. The magnitude of this effect was greatest at the lowest temperature studied, viz., 20°C, and decreased with increasing temperature until it was non-existent at 80°C. It was considered that this effect was due to nonequilibration of the desorption isotherm so that the adsorption isotherms are more likely to represent the true equilibrium, and will be used henceforth as such. The reproducibility of the system was demonstrated by the constancy of the isotherm over a large number of experiments using several different palladium pellets. The isotherms for the skeletal adsorption of hydrogen on to the surface species derived from propene, cyclo-propane, or 1-pentene were each determined at 10°C intervals in the range 20–80°C, and within the limitations of the experiment, which can be assessed from Fig. 2, no differences could be detected.

On plotting the isotherms as log θ versus log p, straight lines were obtained to about $\theta = 0.85$. Furthermore, the slope of these lines was accurately 0.5. The form of the adsorption isotherm can therefore be written thus

$$\theta = K p^{\frac{1}{2}}_{H_2}(0.2 < \theta < 0.85). \qquad (1)$$

The isosteric heat of skeletal adsorption of hydrogen $\Delta H_\theta{}^*$, was determined from the best fit isotherms by plotting the results according to the Clausius–Clapeyron Equation, viz.,

$$\frac{\Delta H_\theta}{R} = \frac{H_g - H_\theta}{R} = \left(\frac{\partial(\ln p)}{\partial 1/T}\right)_\theta,$$

where H_g is the molar heat content of gaseous hydrogen and H_θ is the differential heat content of the adsorbed hydrogen. p is the hydrogen pressure, while T and R are, respectively, the absolute temperature

* All thermodynamic quantities used in this paper will refer to a mole of gaseous hydrogen, H_2.

and the gas constant. The resulting iso-steres were linear at all coverages in the accessible range ($\theta = 0.2$–0.9) and the isosteric heat of adsorption was 12.5 ± 0.5 kcal mole^{-1} and independent of θ. As the equilibrium is quite rapid and only occurs with substantial pressures of hydrogen (>0.1 Torr), it is believed that hydrogenation occurs uniformly throughout the bulk of the porous pellet. It is, therefore, considered unlikely that the constancy of the isosteric heat of adsorption at all degrees of fractional saturation is an artefact of the experiment but is indeed a real effect.

Kinetics of Isotope Exchange

The surface species derived from 1-pentene adsorption was chosen for this study as previous results had indicated that it was more strongly adsorbed than either propene or cyclopropane. Furthermore, its spectrum was more intense, which ultimately leads to greater accuracy. After adsorption of the olefin and preparation of the adsorbed species in the usual way the system was cooled to $< -20°$C in ~50 Torr of hydrogen and evacuated to 1–1.5 Torr; 100 Torr of deuterium was then admitted at this temperature. Under these conditions no dehydrogenation and deuteration of the original hydrogenated species occurred.

The sample was warmed to the desired temperature within the range 40–80°C and maintained there to within $\pm 1°$C while the ν_{C-H} and ν_{C-D} regions of the spectrum were scanned at suitable time intervals. Typical spectra for the exchange reaction at 60°C are shown in Fig. 3. As with skeletal adsorption, exchange occurred without bias toward any functional group in the adsorbed species. The amount of product corresponding to complete exchange was determined by evacuating the cell for about 30 sec and admitting a second dose of 100 Torr of deuterium. By repeating this procedure with hydrogen, the reverse exchange of the chemisorbed perdeuterocarbon with hydrogen could also be followed.

The disappearance of parent and the formation of exchange product followed the respective first-order kinetic equations:
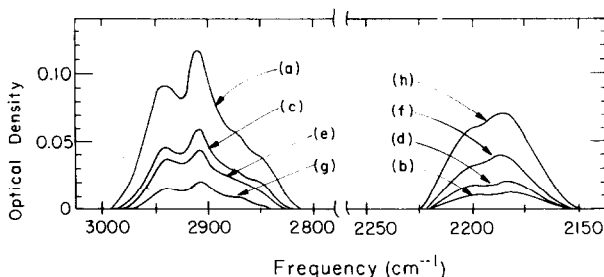
FIG. 3. Infrared spectra obtained during the exchange at 60°C, of the fully hydrogenated adsorbed species derived from 1-pentene adsorption: (a), initial spectrum; (b), after 12 min; (c), 17 min; (d), 27 min; (f), 33 min; (g), 38 min; (h), complete exchange.

$$\log(x_t/x_0) = -kt/2.303 \qquad (2)$$

and

$$\log[(x_\infty - x_t)/x_\infty] = -kt/2.303, \qquad (3)$$

where x is the optical density of the appropriate ν_{C-H} or ν_{C-D} band. Typical examples of these plots for both the hydrogen and deuterium exchange reactions at 60°C are shown in Fig. 4. Arrhenius plots for the effect of temperature on these rate constants are shown in Fig. 5.

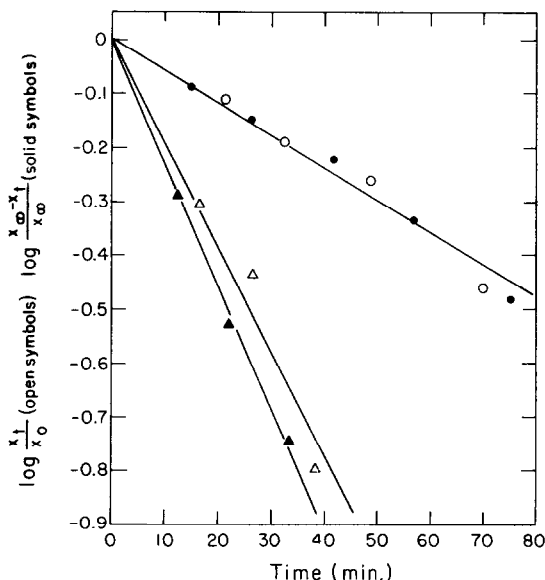The experimental range in rate constants determined from Eqs. (2) and (3) are
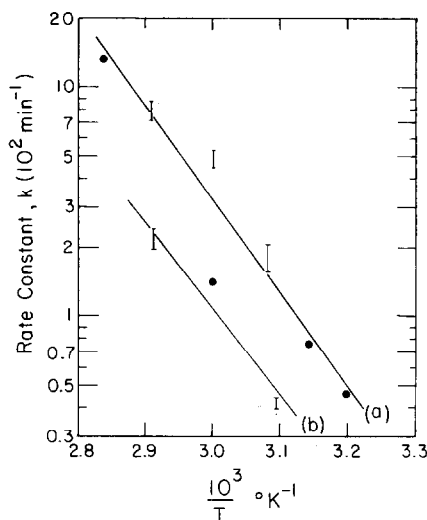

FIG. 5. Arrhenius plots for the effect of temperature on the first-order rate constants determined from Eqs. (2) and (3): (a), exchange of the adsorbed hydrocarbon with deuterium; (b), exchange of the corresponding adsorbed perdeutero species with hydrogen.

shown as error bars in this plot. Both exchange reactions proceeded with an activation energy of 18 ± 1 kcal mole^{-1}. A kinetic isotope effect was apparent such that the exchange of chemisorbed hydrocarbons with deuterium proceeded three times faster than the reverse reaction. Absolute preexponential factors could not be deduced since the techniques employed in this study did not permit a determination of the number of molecules involved.


FIG. 4. Exchange of the adsorbed hydrocarbon with deuterium ($\triangle$) and the reverse exchange of the corresponding perdeutero species with hydrogen ($\bigcirc$) at 60°C plotted according to Eqs. (2) (open symbols) and (3) (solid symbols).

DISCUSSION

The form of the isotherm for the skeletal adsorption of hydrogen, viz., $\theta \propto p^{1/2}_{H_2}$

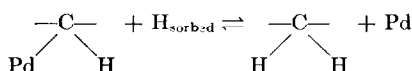$(0.2 < \theta < 0.85)$ shows that adsorption occurs by the prior dissociation of hydrogen, thus

$$H_2 \rightleftharpoons 2H_{sorbed}$$
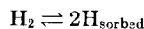
followed by the stepwise introduction of hydrogen into the adsorbed species. In the case of a non terminal carbon atom, this can be written as follows
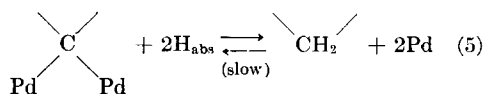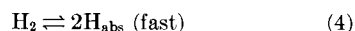
$$\underset{Pd \quad Pd}{-C-} + H_{sorbed} \rightleftharpoons \underset{Pd \quad H}{-C-} + Pd$$

and
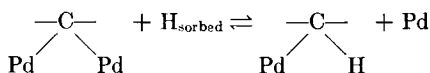
$$\underset{Pd \quad H}{-C-} + H_{sorbed} \rightleftharpoons \underset{H \quad H}{-C-} + Pd$$

The functions of the palladium are therefore first to sorb hydrogen reversibly and dissociatively and second to make and break Pd–C σ-bonds. Furthermore, it is essential that the breaking of Pd–C σ-bonds does not become so extensive that desorption of the adsorbed species occurs.

Under these conditions, a fraction of the adsorbed carbon atoms remain unavailable for the skeletal adsorption of hydrogen. The functions of the palladium substrate are therefore very specific, and it is not surprising that other metals do not behave in a comparable way. For example, over nickel and platinum the skeletal adsorption of hydrogen is more sluggish, less reproducible, and occurs only at considerably higher pressures of hydrogen (6). Furthermore, it is more difficult to dehydrogenate the adsorbed species completely, particularly over nickel, and desorption usually accompanies extensive evacuation. The different behavior with palladium can be attributed at least in part to its unique ability to absorb hydrogen into its bulk rapidly and reversibly (in the pressure range of present interest). The form of the adsorption isotherm for skeletal adsorption [Eq. (1)] is consistent with the involvement of interstitially absorbed hydrogen since absorption of hydrogen into the α phase of palladium hydride (which is the phase relevant to the temperature and pressure conditions of the present experiment) also occurs with the same half-order dependence on hydrogen pressure (8).

An alternative form of sorbed hydrogen was identified in a previous study (7) as being irreversibly adsorbed and responsible for the irreversible perturbation of the ν_{C-H} bands to lower frequencies on initial hydrogenation. This form of hydrogen could not be desorbed at 80°C (the highest temperature studied), and is consequently unlikely to be involved as an intermediate in the skeletal adsorption of hydrogen. In the absence of any evidence for a weakly bonded form of dissociatively chemisorbed hydrogen, the suggestion that interstitially absorbed hydrogen is the precursor to skeletal adsorption appears to be the most reasonable.

Rewriting the overall reaction for the nonterminal carbon atoms of the adsorbed species thus

$$H_2 \rightleftharpoons 2H_{abs} \quad \text{(fast)} \tag{4}$$

$$\underset{Pd \quad Pd}{\diagup C \diagdown} + 2H_{abs} \underset{\text{(slow)}}{\overset{\longrightarrow}{\longleftarrow}} \diagdown CH_2 \diagup + 2Pd \tag{5}$$

and pursuing the suggestion that the sorbed hydrogen is interstitially absorbed, a potential energy diagram can be constructed to describe the detailed energetics of the skeletal adsorption process (Fig. 6). The heat of absorption of hydrogen under the present conditions of pressure and temper-
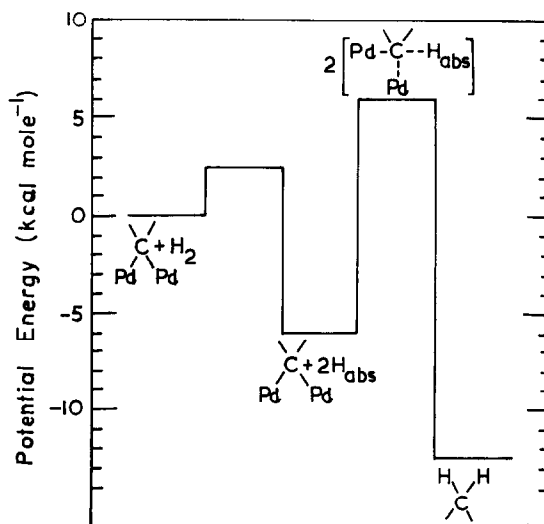

FIG. 6. Potential energy diagram for the skeletal adsorption of hydrogen by an adsorbed linear species on palladium.

ature has been shown to be 6 kcal mole⁻¹ (8) and furthermore occurs with a low activation energy, viz., 2–3 kcal mole⁻¹ (9).

The heat of skeletal adsorption of hydrogen was determined in this study to be 12.5 kcal mole⁻¹, in which case the heat of absorbed hydrogen entering the carbon skeleton, viz., ΔH_5, must be 6.5 kcal mole⁻¹. The mechanism of skeletal adsorption expressed by eqs. 4 and 5 also provides an acceptable mechanism for exchange when deuterium is substituted for hydrogen. The exchange mechanism then is similar to the repeated second-point adsorption mechanism for ethane-deuterium exchange over metal films (10), except that the ultimate equilibrium of the adsorbed hydrocarbon with the gas phase does not occur. Under these conditions, the activation barrier for exchange will be similar to that for skeletal adsorption and a common activated complex, designated

$$\underset{\diagdown}{C} \text{------} H_{abs}'$$
$$\diagdown Pd$$
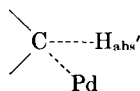
can be described. The possibility of hydrogen absorption [Eq. (4)] controlling the rate of reaction can be rejected by comparing its rate with the overall rate of exchange. Thus it is found that hydrogen absorption and exchange in palladium black is measurable at −190°C (9), whereas the rate of skeletal hydrogen exchange was only just measurable at 40°C. More specifically the rate controlling step can be identified with the reverse reaction of Eq. (5) on the basis of the kinetic isotope effect observed during exchange. The magnitude of this effect (viz., ~3) is just that expected for the relative rates of C–H to C–D bond rupture (11). The competitive effect due to a similar difference between absorbed hydrogen and deuterium is considered to be trivial, because of the expected smaller zero point energy difference in this case. An overall activation energy of 5.5 kcal mole⁻¹ for skeletal adsorption of hydrogen compared with 18 kcal mole⁻¹ for desorption is consistent with the non-equilibrium hysteresis of the adsorption isotherms (Fig. 2).

The heat content of the overall adsorption of skeletally adsorbed hydrogen can be written thus

$$q = 2E(\text{C–H}) - 2E(\text{Pd–C}) - E(\text{H–H})$$

and according to Pauling's expression

$$E(\text{Pd–C}) = \tfrac{1}{2}[E(\text{Pd–Pd}) + E(\text{C–C})] + 2.3(\chi_{Pd} - \chi_C)^2,$$

taking

$$E(\text{C–H}) = 99 \text{ kcal mole}^{-1},$$
$$E(\text{H–H}) = 104 \text{ kcal mole}^{-1},$$
$$E(\text{C–C}) = 79 \text{ kcal mole}^{-1},$$
$$E(\text{Pd–Pd}) = \frac{\Delta H \text{ sublimation}}{6} = \frac{118}{6}$$
$$= 19.7 \text{ kcal mole}^{-1},$$
$$\chi_{Pd} = 2.2,$$

and

$$\chi_C = 2.5, \, q \text{ becomes } -10 \text{ kcal mole}^{-1},$$

or

$$\Delta H = 10 \text{ kcal mole}^{-1}.$$

This result is in reasonable agreement with the observed figure of 12.5 kcal mole⁻¹ and further supports the view that dehydrogenation and related processes occur by Pd–C σ-bond formation.

In a study of the exchange of gaseous n-hexane with deuterium over evaporated palladium films (12), it has been shown that the activation energy (18 kcal mole⁻¹) and the kinetic isotope effect (3–4) were identical to those found in the present study. In the original study of the n-hexane exchange over evaporated palladium films (13), it was concluded that the adsorbed species was multiply bonded to the surface, although it was not possible to distinguish between bonding with multiple Pd–C σ-bonds, or alternatively by multicenter π-bonding through several adjacent sp^2 hybridized carbon atoms, as was suggested to explain the exchange characteristics of the polymethylcyclopentanes (14).

In view of the apparent similarity in the mechanism of n-hexane exchange with the reaction of present interest the absence of

any evidence of a change in hybridization of the adsorbed species would appear to suggest that alkane–deuterium exchange may be better written according to the existing repeated second-point adsorption mechanism involving Pd–C σ-bonds. As previously discussed (7), it is significant that although n-hexane is multiply bonded to the surface during exchange the adsorbed species is still in equilibrium with the gas phase and can be desorbed. Since the adsorbed species involved in the present study were not in measurable equilibrium with the gas phase, it was concluded that they must be even more extensively bonded to the surface. Thus, if the step common to the exchange of gaseous alkanes and irreversibly adsorbed olefins, viz., the hydrogenation of a Pd–C σ-bond, are mechanistically similar and involve the same heat (12.5 kcal mole^{-1}), the latter adsorbed species must be more extensively bonded to the surface by an amount dependent on the greater heat of adsorption of an olefin compared with an alkane.

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