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Heterogeneous Catalysis in Organic Chemistry. 2.[1] A Mechanistic Comparison of Noble-Metal Catalysts in Olefin Hydrogenation

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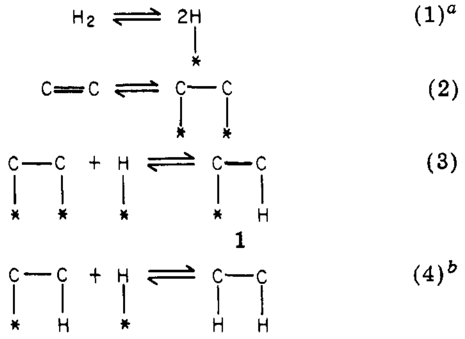
Product stereochemistry, double-bond isomerization, deuterium incorporation, and hydrogen uptake data were obtained for the hydrogenation/deuteration of a number of cyclic olefins over the various supported noble-metal catalysts. The data from the Pt-catalyzed reactions are in substantial agreement with previously reported results that have been explained by the Horiuti–Polanyi mechanism. It was also found that while rhodium was similar to platinum in its reaction characteristics, it is more susceptible to steric factors and there is more equilibration of the half-hydrogenated state than is observed with platinum. Olefin hydrogenations over palladium are quite different, taking place by way of a π-allyl-absorbed species rather than the 1,2-σ_2 entity utilized in the Horiuti–Polanyi process. Limited data indicate that while the use of ruthenium gives anomolous results, iridium appears to be mechanistically similar to platinum.

Catalytic hydrogenation is a well-established method for the reduction of a variety of functional groups. The successful utilization of this technique, though, requires the proper selection of a number of reaction variables such as the quantitiy and type of catalyst, solvent, concentration of the substrate, temperature, and hydrogen pressure. The selection of these parameters is usually based on conditions reported for comparable reactions or the discussions of reaction variables and generalized "recipes" found in reviews and monographs[2] on the subject. While this approach is generally quite successful in hydrogenations involving a straightforward transformation, in those hydrogenations in which product selectivity or stereoselectivity is desired, more care must be exercised in the selection of the reaction variables used. As with other reactions, a knowledge of the reaction mechanism and the effect of a change in reaction variables on that mechanism should be of value in making the proper choice of reaction conditions to affect the desired selectivity in a hydrogenation reaction.

Unfortunately this type of mechanistic understanding is available for the hydrogenation of only a few functional groups, the most widely studied being the hydrogenation of a double bond. The mechanism for this reaction is shown in Scheme I. The mechanism was first proposed in 1934[3] and, with only slight modifications, is still generally accepted. It accounts readily for the differences observed in product stereochemistry resulting from changes in hydrogen availability to the catalyst[4] as well as concurrent double-bond isomerization[5] and deuterium incorporation and exchange found in products and recovered olefins.[6] One aspect of this reaction that is not obvious from this mechanism is the effect that specific catalysts can have on the outcome of the hydrogenation. Although various metal catalysts can be used in the conversion of an alkene to an alkane, they do so to differing degrees of intermediate isomerization, deuterium incorporation and exchange, and, where applicable, product stereochemistry.[2]

Scheme I[3]



[a] The asterisk (*) indicates adsorption on a metal surface. [b] This step is considered to be irreversible under the common solution-phase olefin hydrogenation conditions: room temperature and low pressure. Reversal is noted, though, in vapor-phase reactions and solution reactions run at higher temperature.

A number of studies has been reported for the comparison of various metal catalysts, particularly the noble metals, in the saturation of double bonds.[7-10] These have been concerned with product stereochemistry differences, double-bond isomerizations, reaction rates, and deuterium exchange but not all on the same system. In addition various forms of catalysts such as reduced oxides, metal blacks, and supported metals were used, frequently interchangeably and not always in the same amount. Ethanol and acetic acid were the common solvents used, sometimes both in the same study. Occasionally, solvent data were not given. Further, different types of apparatus were used, so even in a comparison of similar hydrogenations marked differences could be present because of variations in the rate of hydrogen diffusion to the catalyst

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that is a function of reactor design and agitation.

Since all of these factors are known to have an effect on hydrogenation reactions, the effective correlation of the reported results to obtain a meaningful comparison of the various catalysts studied is not really possible.

To clarify this situation and to establish a more realistic basis for a comparison of metal catalysts in the hydrogenation of double bond, the hydrogenations and deuterations of a number of cyclic olefins were run and all aspects of the reaction, product stereochemistry, relative rates, double-bond isomerization, and deuterium incorporation and exchange, were investigated by using a standard set of reaction conditions. The olefins were hydrogenated in a dilute absolute ethanol solution at a fixed high olefin:catalyst ratio. The rate of agitation was held constant for each series of reactions. The catalysts used were aged, commercially available 5% noble metal on carbon species. Raney nickel catalysts were not included because it was reported that the product stereochemistry obtained on hydrogenation of cyclic olefins over these catalysts was dependent on the past history of the Raney nickel.[11] This was not the case with the supported noble metals used.

Experimental Section

Gas chromatographic separations were accomplished by using a 45 ft × 1/4 in. 10% ethylene glycol succinate on Chromosorb P column at 130 °C and a He flow rate of 48 mL/min: retention times (minutes): methylcyclohexane (**10**), 20; methylenecyclohexane (**6**) 22; 4-methylcyclohexene (**9**), 25; 3-methylcyclohexene (**8**), 25; 1-methylcyclohexene (**7**), 26; *trans*-4-*tert*-butylmethylcyclohexane (**5**), 38; *cis*-4-*tert*-butylmethylcyclohexane (**4**), 44; 4-*tert*-butylmethylenecyclohexane (**2**), 55; 4-tert-butylmethylcyclohexene (**3**), 58.

Materials. The catalysts were aged, 5% metal on carbon obtained from Engelhard Industries. The hydrogen used was passed through a Deoxo unit and a drying tower before use. The methylcyclohexenes and methylenecyclohexane were obtained from Aldrich Chemical Co., distilled twice, and checked for purity by GC analysis. All olefins except those used in the pressure-dependent stereochemistry study were perculated through an alumina column for 10 min with dry N_2 immediately before use. This pretreatment was essential for obtaining reproducible rate data, but it had no effect on product stereochemistry. The ethanol solvent was absolute and was distilled from sodium before use. The EtOD, obtained from Aldrich Chemical Co., was 99.5+ atom % D and was used as received. The D_2, obtained from Matheson, was at least 99.5% pure and was also used as received.

4-*tert*-Butylmethylcyclohexene (3) was prepared by the reaction of methylmagnesium iodide with 4-tert-butylcyclohexanone followed by acid-catalyzed dehydration of the resulting alcohol:[5a] bp 195-197 °C (lit.[5a] bp 196–197 °C).

4-*tert*-Butylmethylenecyclohexane (2) was prepared from methyltriphenylphosphonium bromide and 4-*tert*-butylcyclohexanone by a modified Wittig reaction:[12] bp 124–125 °C (30 mm) (lit.[12] bp 78–80 °C (18 mm).

Variable-pressure hydrogenations were run in a glass-lined Autoclave Engineers 300-cm^3 MagneDrive autoclave. The catalyst (50 mg), 20 mL of anhydrous ethanol, and 0.50 mL of olefin were placed in the glass liner, and the autoclave was closed. The system was flushed with hydrogen three times and the pressure adjusted to the desired value. For atmospheric pressure runs in this reactor the vent line from the autoclave was opened and connected to a glycerol bubbler. The reactions, except those over iridium, were run to essentially complete saturation at room temperature and a constant stirring speed for all reactions. The catalyst was removed by filtration and the filtrate analyzed by gas chromatography.

Atmospheric pressure hydrogenation and deuterations were run on a sloping manifold apparatus[13a] and a 50-mL jacketed flask with a thermometer well and a side arm fitted with a septum adapter as the reactor.[13b] After the addition of 50 mg of catalyst and 20 mL of anhydrous ethanol the reactor was connected to the hydrogenation apparatus and the system alternately evacuated and filled with hydrogen three times. The internal pressure was adjusted to atmospheric pressure, and the catalyst and solvent were stirred for 10 min with a magnetic stirrer at a fixed setting. After equalization of the pressure, 0.50 mL of olefin was injected into the reactor through the septum and the rate of hydrogen uptake measured by using the technique previously described.[13c] The reaction was continued until about 25% of the theoretical hydrogen or deuterium was absorbed after which time the catalyst was removed by filtration and the filtrate analyzed by gas chromatography.

The deuterations were run in an identical manner using EtOD as the solvent. After removal of the catalyst the filtrate was poured into water and extracted thoroughly with pentane. After being dried, the pentane solution was concentrated and subjected to GC–MS analysis. Reported isotopic distributions are corrected for natural isotope abundance. Samples of the solvent were stirred in a deuterium atmosphere over each of the catalysts for times comparable to those encountered for olefin hydrogenations. ^1H NMR analysis of the solvent after this treatment showed that no deuterium exchange occurred over any of the catalysts.

Each experiment was carried out at least twice with the hydrogen uptake data reproducible to within $\pm 0.2 \times 10^{-4}$ mL/min/mg of metal and the product composition to within ±1%.

Results

Previous studies[8] of the pressure effect on the stereochemistry of the hydrogenation of 4-*tert*-butylmethylenecyclohexane (**2**) and 4-*tert*-butylmethylcyclohexene (**3**) over platinum led to the conclusions that under conditions that promote a high hydrogen availability to the catalyst (rapid agitation, small catalyst quantities, and/or high pressure) the product-determining step is the adsorption of the olefin on the catalyst (step 2, Scheme I). Under these conditions little, if any, olefin desorption takes place and the cis:trans (4:5) ratio of saturated products is determined by the difference in steric constraints shown on contact of each face of the double bond with the catalyst surface. Under conditions of low hydrogen availability both the olefin adsorption and half-hydrogenated state formation steps (steps 2 and 3) are reversible and the product-determining step is the saturation of the half-hydrogenated state (step 4).

While these results were important in developing an understanding of the olefin hydrogenation reaction over platinum, the extension of these conclusions to other catalysts was based only on data obtained at atmospheric pressure. To provide a correlation with previous work and to determine the effect of hydrogen availability on olefin saturation over other catalysts, the hydrogenation of **2** was run under several hydrogen pressures and at constant agitation over each of the noble-metal catalysts platinum, rhodium, palladium, ruthenium, and iridium. The percentages of the cis product 4 obtained in each of these reactions are shown in Figure 1.

In agreement with previous results[8] the amounts of 4 formed over platinum decreased as the pressure increased. A similar trend was also noted with iridium. Over rhodium and ruthenium there does not appear to be any change while over palladium the amount of 4 produced increased with increasing hydrogen pressure. The fact that the changes observed in this present work were not as great as those reported previously was not unexpected. Not only was a different solvent used but also the reactor used here provided a very vigorous agitation, and this, along with the

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[13] (a) Reference 2a, p 12. (b) Reference 2a, p 20. (c) Reference 2a, p 18.

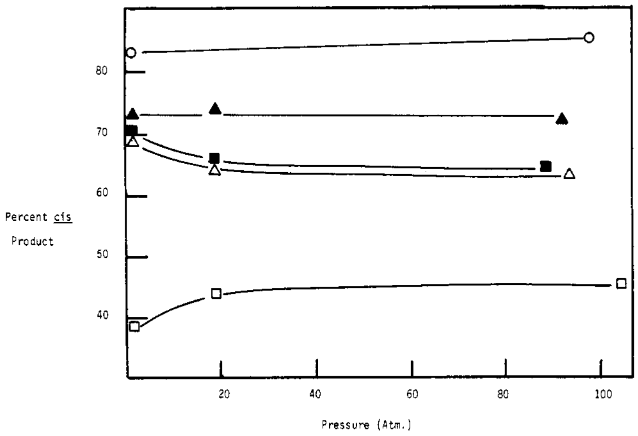


Figure 1. Pressure effect on the product stereochemistry in the hydrogenation of 2: ■, Pt/C; ▲, Rh/C; □, Pd/C; ○, Ru/C; △, Ir/C.

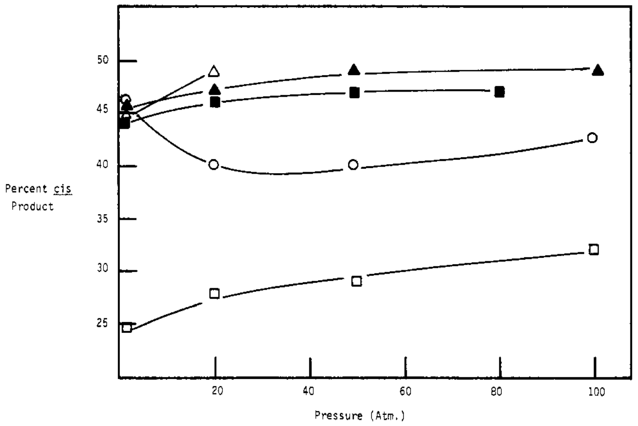


Figure 2. Pressure effect on the product stereochemistry in the hydrogenation of 3: ■, Pt/C; ▲, Rh/C; □, Pd/C; ○, Ru/C; △, Ir/C.

Table I. Hydrogen of 2 under Low Hydrogen Availability Conditions[a]

catalyst[b]	% 4[c]	catalyst[b]	% 4[c]
5% Pt/C	71	5% Ir/C	74[f]
5% Pt/C[d]	74	5% Ru/C	78[g]
PtO$_2$[e]	76	5% Pd/C	35
5% Rh/C	77		

[a] Atmospheric pressure; magnetic stirring. [b] 50 mg unless otherwise noted. [c] ±1%. [d] 250 mg. [e] Equivalent to 12.5 mg of Pt. [f] Reaction only went to 50% completion. [g] Reaction only went to 35% completion.

use of a high olefin: catalyst ratio, increased the hydrogen availability to the catalyst, even at low hydrogen pressures. To show the effect of low hydrogen availability to these catalysts 2 was hydrogenated over each of them using a magnetically stirred reactor at atmospheric pressure. The results obtained are listed in Table I. These data show that over rhodium a decrease in hydrogen availability resulted in an increase in the amount of 4 formed as were observed with both platinum and iridium while over ruthenium the amount of 4 produced decreased.

The stereochemical data obtained over palladium appear to be quite similar to the pressure–stereochemistry relationship previously found for the hydrogenation of 3 over platinum[8] (see also Figure 2). This was not unexpected since it is well-known that palladium readily promotes double-bond isomerization and almost all of the differences observed between platinum and palladium have been attributed to this facile isomerization capability.

To check the assumption that the products obtained on hydrogenation of 2 over palladium were actually formed by the hydrogenation of 3, which was formed by isomerization, the effect of pressure on the product stereochemistry obtained on hydrogenation of 3 was determined for reactions run over palladium and the other noble-metal catlysts as well. The results are shown in Figure 2. Again, in agreement with previously reported results,[8] the amount of the cis product 4 formed on hydrogenation of 3 over platinum decreased with decreasing hydrogen availability. Similar trends were also noted with both rhodium and iridium, while over ruthenium the amount of 4 formed went through a minimum as the hydrogen pressure increased. Over palladium the amount of 4 formed increased with increasing hydrogen pressure just as was observed in the hydrogenation of 2 but considerably less of the cis product was formed from 3 than was obtained on hydrogenation of 2.

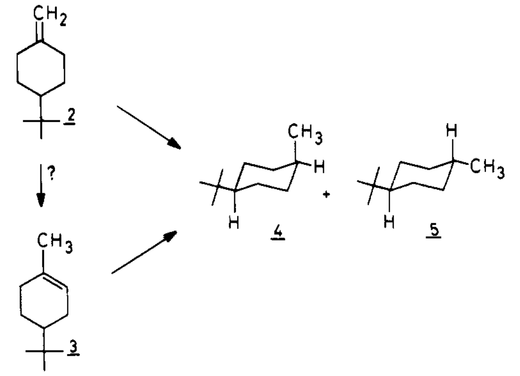
Table II. Rates of Hydrogen Uptake in the Hydrogenation of Isomeric Methycyclohexenes

	hydrogen uptake[a]			
catalyst	6	7	8	9
Pt/C	7.3	5.5	5.9	6.1
Rh/C	8.7	5.6	7.4	9.4
Pd/C	5.9	6.1	5.9	6.1

[a] (mL/min/mg of metal) $\times 10^4 \pm 0.2$.

Table III. Percent of 7 Present in Olefinic Fraction Recovered after Partial Hydrogenation[a]

catalyst	6	8	9
Pt/C	62	19	12
Rh/C	32	9	7
Pd/C	100	34	37



The hydrogenations run over irridium and ruthenium were very sluggish with these catalysts being 50–150 times less active than platinum, rhodium, or palladium. This, plus the fact that neither irridium nor ruthenium are common hydrogenation catalysts, prompted the decision not to include them in further phases of this study.

To provide further information concerning the double-bond isomerization and to remove product stereochemistry from consideration, attention was shifted to the hydrogenation of methylenecyclohexane (6), methylcyclohexene (7), 3-methylcyclohexene (8), and 4-methylcyclohexene (9). The initial rates of hydrogen uptake observed on saturation of each of these compounds over platinum, rhodium, and palladium are given in Table II. On partial hydrogenation of 6, 8, and 9, the recovered olefinic material invariably contained some of the more stable isomer 7. In Table III are given the amounts of 7 formed when the hydrogenations of 6, 8, and 9 were stopped after 25% completion. A measure of the tendency of 9 to isomerize to 8 and vice versa was not obtainable since these two compounds were not separable with the gas chromatographic conditions used.

Table IV. Isotopic Distribution from Molecular Ion and M – CH_3 Regions of the Mass Spectra of Methylcyclohexane Obtained on 25% Deuteration

		methylcyclohexane 10								M – CH_3							
catalyst	starting olefin	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_{av}	d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_{av}
Pt/C	**6**	4	20	54	14	6	1		1.99	21	75	3	1				0.84
Rh/C	**6**	23	33	24	11	4	4	1	1.56	48	48	3	1	1			0.57
Pd/C	**6**	55	29	10	4	1			0.65	73	20	5	1				0.33
Pt/C	**7**	3	15	37	21	10	11	3	2.65	7	26	47	13	5	2	1	1.95
Rh/C	**7**		na[a]								na[a]						
Pd/C	**7**	32	24	11	5	2	24	2	2.01	53	29	11	2	1	1		0.82
Pt/C	**9**	25	29	29	11	3	1	1	1.50	29	30	28	9	3	1		1.30
Rh/C	**9**	25	34	25	10	4	1	1	1.48	27	33	25	9	3	1		1.27
Pd/C	**9**	38	32	21	7	2	1		1.08	41	31	20	6	2	1		1.02

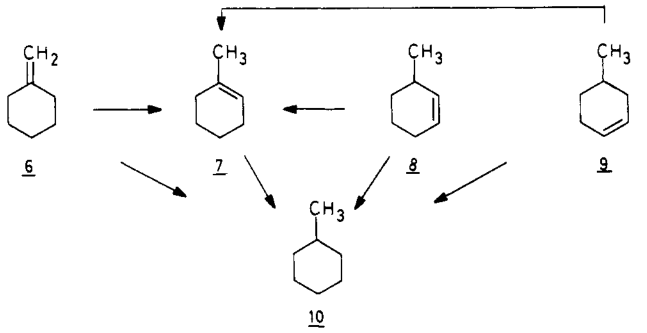
[a] na = not available.

Table V. Isotopic Distribution in Recovered Starting Materials and Isomerized Olefins on 25% Deuteration

		recovered starting material						**7** formed from isomerization					
catalyst	olefin	d_0	d_1	d_2	d_3	d_4	d_{av}	d_0	d_1	d_2	d_3	d_4	d_{av}
Pt/C	**6**	86	11	2	1	1	0.22	na					
Rh/C	**6**	78	18	4			0.26	47	29	15	7	1	0.84
Pd/C	**6**		na[a]					59	28	11	3		0.59
Pt/C	**7**	89	10	1			0.12						
Rh/C	**7**	91	8	1			1.10						
Pd/C	**7**	45	32	15	5	2	0.90						
Pt/C	**9**[b]	78	17	4	1		0.28	72	19	6	2	1	0.41
Rh/C	**9**[b]	69	23	6	2	1	0.45	74	15	6	3	1	0.45
Pd/C	**9**[b]	54	34	10	2		0.60	82	14	4			0.22

[a] No **6** present in reaction medium. na = not available. [b] Recovered starting material includes both **8** and **9**.

The deuterations of **6**, **7**, and **9** were also investigated to provide information concerning the relative extent of step reversal in the Horiuti–Polanyi mechanism over each of these catalysts. Further, since the product of these reactions methylcyclohexane (**10**) loses the methyl group on mass spectral fragmentation,[14] evaluation of the M–CH_3 region of the mass spectra of **10** produced in these deuterations can provide data concerning the extent to which deuterium exchange has taken place on the side chain. In Tables IV and V are shown the isotopic distributions of the product **10**, the M–CH_3 region from **10**, the recovered starting material, and, from **6** and **9**, **7** that was formed by double-bond isomerization. These data are for reactions run to 25% completion over platinum, palladium, and rhodium.



Discussion

Platinum. Most of the mechanistic studies of the hydrogenations of a double bond have involved reactions run over platinum catalysts. These studies have led to the general acceptance of the Horiuti–Polanyi mechanism shown in the Scheme I[3] for this reaction. The data shown in Figures 1 and 2 concerning the pressure effect on the stereochemistry of the products obtained on hydrogenation of **2** and **3** over platinum are in general agreement with the reported trends.[8] Duplication of previously reported results obtained over this catalyst could readily be accomplished by making the appropriate changes in the standard reaction conditions used in this present study. Examples of the effect of such changes on the amount of the cis product **4** obtained on the hydrogenation of **2** under low hydrogen availability conditions are shown in Table I. The difference between these data and reported values is due to the use of ethanol as the solvent in the present instance and acetic acid in the earlier studies. Repetition of the platinum oxide catalyzed reaction using acetic acid as the solvent gave a product mixture in agreement with the reported value.

The increase in the amount of **4** formed over the larger quantities of catalyst is another indication of the influence of hydrogen availability on product stereochemistry. When a standard, magnetically stirred, hydrogenation apparatus[13a] is used, the amount of hydrogen available to the catalyst is limited by its diffusion through the reaction medium. Increasing the amount of catalyst present under such conditions will decrease the H:active site ratio or, put in another way, will lower the hydrogen availability per active site. Under such low hydrogen availability conditions the product-determining step in olefin hydrogenation is step 4 in the Horiuti–Polanyi mechanism[3] (Scheme I). Increasing the hydrogen availability by decreasing the amount of catalyst, increasing the rate of agitation and/or the hydrogen pressure shifts the product-determining step to the olefin adsorption (step 2, Scheme I) so that factors influencing adsorption on one or the other face of the double bond become more important.

The extent of double-bond isomerization observed on hydrogenation of **6**, **7**, and **8** over Pt/C (Table III), the primary formation of the d_2-saturated species on deuteration of **6** and **7**, and the slight deuterium exchange noted in the recovered olefins (Table V) are all in agreement with reported observations.[5-10] The deuteration of **9**, however,

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[14] Meyerson, S.; Nevitt, T. D.; Rylander, P. N. In "Advances in Mass Spectrometry"; Pergamon Press: Oxford, 1963; Vol. 2; p 313.

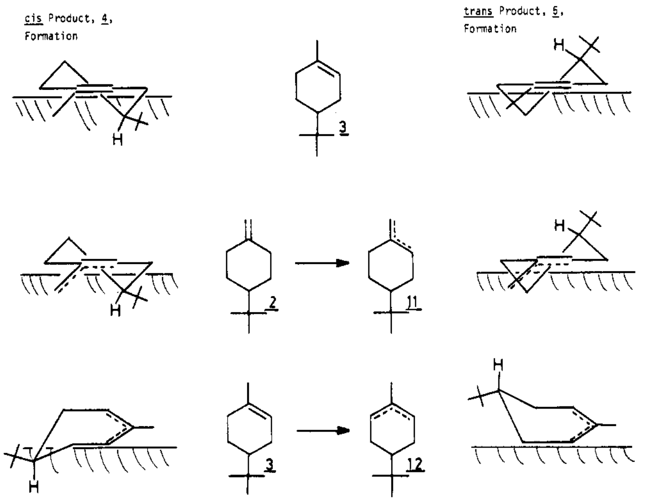

Figure 3. Modes of adsorption of methylcyclohexene π-allyls.

resulted in a lower deuterium incorporation than was observed in the deuteration of 7. In addition the product contained almost equal amounts of the d_0, d_1, and d_2 species. Such results are indicative of a fairly large amount of double-bond isomerization taking place with this olefin. This should not be unexpected with 9 since with this material there is available by isomerization four disubstituted olefinic species: the two equivalent Δ^3 compounds 9 and the two equivalent Δ^2 species 8. Unfortunately, separation of 8 and 9 was not possible with the gas chromatographic conditions used even though a considerable effort was made to do so. Further support for this isomerization comes from the identical rates of hydrogenation of 8 and 9 over Pt/C as shown in Table II.

Comparison of the deuterium incorporation data for the methylcyclohexane produced in these deuterations with the M–CH_3 fragment (Table IV) shows that on deuteration of the exocyclic methylene group in 6, as expected, an average of one deuterium is found on the methyl group of the product. A fair amount of exchange also occurs on the methyl group during the deuteration of 7 but not in the deuteration of 9.

Because of the general agreement of these results with the previously reported work these platinum data were used as the standard against which the results obtained with the other catalysts were compared.

Rhodium. The data in Figures 1 and 2 show that the hydrogenation of both 2 and 3 over rhodium gave more of the cis product 4 than was obtained over platinum. The pressure variation data for the hydrogenation of 3 over rhodium paralleled the data obtained with platinum (Figure 3). Product stereochemistry data similar to that found for the atmospheric pressure hydrogenation of 3 has been reported for the hydrogenation of a number of 1,4-dialkylcyclohexenes over Rh/C.[7b,10d] There was no influence of pressure on the product stereochemistry observed in the hydrogenation of 2 over rhodium with reactions run with rapid agitation. However, when this hydrogenation was repeated at atmospheric pressure under low hydrogen availability conditions, the amount of 4 produced increased to 77% (Table I), again showing a parallel with the platinum data.

It appears from this similarity that olefin hydrogenations run over rhodium are comparable mechanistically to the platinum-catalyzed reactions. The formation of slightly more of the cis product 4 over rhodium could be a result of shorter metal–substrate bonds that would accentuate steric crowding in the absorbed state. A further manifestation of this increased steric susceptibility with rhodium is the change in the rates of hydrogen uptake observed in the hydrogenation of 6, 7, 8, and 9 over rhodium as shown in Table II. Thus, it appears that steric factors play a more important role in the hydrogenation of olefins over rhodium than they do with platinum catalysts.

Rhodium promoted less double-bond isomerization than did platinum (Table III) but generally more deuterium exchange and less d_2 formation in the saturated products were observed with rhodium than with platinum (Table IV). These seemingly contradictory observations can be rationalized by involving a more facile reversal of step 3 of the Horuiti–Polanyi mechanism (Scheme I) and a less ready reversal of step 2 with rhodium than is the case with platinum.

Palladium. It has long been recognized that olefin hydrogenations over palladium are not generally as uncomplicated as those run over platinum. This difference is usually ascribed to the facile double bond isomerization that takes place over palladium, giving a mixture of olefins from which the saturated products are produced.[10] The data in Table III show the extent of this isomerization capability. As seen by the results shown in Figure 1, the pressure effect on product stereochemistry in the hydrogenation of 2 over palladium is different from that noted for the other catalysts; increasing hydrogen availability resulted in an increase in the amount of 4 produced. Since these data are very similar to those obtained on hydrogenation of 3 over platinum (Figure 2), it was first assumed that this was another manifestation of the facile isomerization capability of palladium; 2 had been isomerized to 3 which was then hydrogenated. However, while the hydrogenation of 3 over palladium also showed an increase in cis isomer formation with increasing hydrogen pressure (Figure 2), the amount of 4 formed from 3 at the various pressures used was considerably lower than that formed on hydrogenation of 2 (Figure 1). Thus, the products from the hydrogenation of olefins over palladium are not formed solely by way of an isomerization followed by the saturation of the isomer.

Since π-allyl complexes are formed on reaction of olefins with palladium complexes[15] and π-allyl adsorption has been proposed for hydrocarbon reactions on palladium metal,[16] this seemed to be a logical alternative to the classical 1,2-σ_2 adsorption of the Horiuti–Polanyi mechanism[3] (Scheme I). On the basis of π-allyl complex formation[15] the 7,1,2-π-allyl 11 should be formed from 2 and the 6,1,2 moiety from 3. As seen from Figure 3 11 has essentially the same adsorption stereochemistry as does 3 so hydrogenation of 2 over palladium by way of 11 would be expected to give the same stereochemical results as observed for the hydrogenation of 3 over platinum. On the other hand, the drawings in Figure 3 also indicate that 12 is expected to adsorb in a manner leading to the predominant formation of the trans product as is observed in the hydrogenation of 3 over palladium. Similar high trans isomeric ratios have been reported for the hydrogenation of a number of 1,4-dialkylcyclohexenes over Pd/C.[7b,10d] The formation of the 1,2,3-π-allyl species 13 is not expected on the basis of reported palladium π-allyl complex formation data.[15]

It appears, then, that the peculiar catalytic behavior of palladium can best be accounted for by invoking the intermediacy of a π-allyl-adsorbed species. Further support for this premise comes from the hydrogenation rate data given in Table II. Over palladium all four olefins 6–9 were

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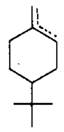
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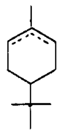
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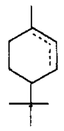
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hydrogenated at essentially the same rate as would be expected if very similar adsorbed species were involved. That these rates were not diffusion limited can be seen by the fact that these same olefins could be hydrogenated under the same conditions over other catalysts at considerably faster rates. The involvement of a π-allyl species also explains the facile isomerization noted with palladium-catalyzed hydrogenations. Since these π-allyl species are formed by the extraction of an allylic hydrogen, this can also account for the marked dilution of the deuterium pool on the catalyst when palladium is used to deuterate double bonds. Thus, deuterations of **6**, **7**, and **9** over palladium give methylcyclohexanes with the d_0 species predominating and little polydeuterated material (Table IV). Recovered olefins show more deuterium exchange than observed with either platinum or rhodium (Table V), as would be expected if a π-allyl intermediate were involved.

One exception to the general absence of much polydeuterated material from these reactions is the presence of a considerable amount of a d_5 species in the methylcyclohexane formed on deuteration of **7** (Table IV). Since this entity was formed only when **7** was deuterated, it was suspected that the excess exchange was taking place on the methyl group through the intermediacy of a 7,1,2-π-allyl similar to **11**. The absence of any appreciable polydeuterated material in the $M-CH_3$ region of the mass spectrum of this product established that these extra deuteria were indeed located on the methyl group. It seems, then, that both the 7,1,2-π-allyl **11** and 6,1,2-π-allyl species **12** are involved in the palladium-catalyzed hydrogenation of 1-methylcyclohexenes.

Ruthenium and Iridium. Because olefin hydrogenations over these catalysts were extremely slow, they were only used in the pressure–stereochemistry studies. The results obtained, while not conclusive, indicate that while it is between 50 and 150 times less reactive than platinum depending on substrate and pressure, iridium is probably mechanistically similar to platinum. Ruthenium, though, is anomalous as shown particularly from the data depicted in Figure 2. Why this behavior occurred is not readily apparent. The fact that the other metals have an *fcc* crystalline arrangement while ruthenium has an *hcp* arrangement could be of some importance. More work is needed before any definitive answer can be given.

Registry No. **2**, 13294-73-0; **3**, 3419-74-7; **6**, 1192-37-6; **7**, 591-49-1; **8**, 591-48-0; **9**, 591-47-9; Pt, 7440-06-4; Rh, 7440-16-6; Pd, 7440-05-3; C, 7440-44-0.

Anodic Oxidation Potentials of Substituted Pyrroles: Derivation and Analysis of Substituent Partial Potentials

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With cyclic voltammetry, anodic oxidation potentials for a series of 117 substituted pyrroles have been measured and analyzed. The pyrroles studied are useful intermediates for the synthesis of polypyrrole pigments, and the information gained is related to reactivity in pyrrole systems and should be applicable to synthetic endeavors. Substituent partial potentials for the various common peripheral groups are derived by using a least-squares analysis and are interpreted. With a few exceptions, on the basis of the derived substituent contributions it is possible to deduce accurate calculated oxidation potentials for virtually any common substituted pyrrole. Calculated and measured oxidation potentials differ in two major circumstances: (a) when two strongly electron-withdrawing substituents are located at the 2- and 5-positions and (b) when an unsubstituted 2-position occurs concomitantly with a strongly electron-withdrawing 5-position substituent. Though correlations between electrochemical substituent partial potentials and standard σ_p and σ_m coefficients are not apparent, a good correlation was obtained between pK_a and oxidation potential for a series of pyrrole-5-carboxylic acids.

Introduction

Pyrroles are "π-excessive" heterocycles[1,2] that are readily oxidized. Several studies of anodic oxidation of pyrroles[3] have been described, and the major thrust in these investigations has been directed toward the formation of "pyrrole black", a stable, flexible "metallic polymer" with p-type conductivity.[4-10] One-electron anodic oxidation of simple pyrroles is irreversible,[3,10] the resulting π-cation radical reacting further either with pyrrole in situ (to give polymers) or with added or adventitious nucleophiles (to give substitution products). For example, anodic oxidation in the presence of methoxide[11] or cyanide[12] affords regioselectively substituted products.[13] Anodic oxidation of polyarylpyrroles has been extensively investigated,[14-20]

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