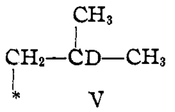
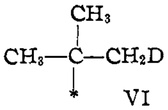
adjacent to the carbon–carbon double bond exerts a steric effect on adsorption to about the same extent whether the double bond is exo- or endocyclic. The ratio of *cis/trans* isomers obtained from each is almost identical at high pressures. The effect is in the nature of a non-bonded interaction between the methyl group attached to the saturated carbon atom and the surface. However, the greater change in *cis/trans* ratio for the 2,3-isomer on going to low pressures suggests that the compressional factors are more pronounced in it than for the *exo* at the "half-hydrogenated state." Perhaps this is related to the greater constraint present in the six-membered cycle when it is adsorbed endocyclic rather than exocyclic. Indeed, in the latter, the cycle is approximately an unstrained chair conformation.

Of the possible transition states which yield the "half-hydrogenated states," those of lowest energy are probably the ones leading to the monoadsorbed hydrocarbon having the least substituted carbon atom. This follows from the experiments of Wilson, Otvos, Stevenson and Wagner[29] who showed that when isobutylene is deuterated, almost no exchange of deuterium for hydrogen is observed in the olefin, although the deuteration and exchange of 1- or 2-butene occurs with comparable rates. They interpreted this to mean that practically all of the "half-hydrogenated state" formed from isobutylene was V rather than VI because the formation of an olefin from VI would of certainty lead to one which contained deuterium. Curiously the same orientation is shown in the addition of boron hydrides to olefins, although in this instance the reaction is effectively irreversible.[30]



$$\underset{*}{CH_2}-\overset{CH_3}{CD}-CH_3$$

V



$$CH_3-\underset{*}{\overset{CH_3}{C}}-CH_2D$$

VI

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[29] J. N. Wilson, J. W. Otvos, D. P. Stevenson and C. D. Wagner, *Ind. Eng. Chem.*, **45**, 1480 (1953).

[30] H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **81**, 6423 (1959).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARKANSAS, FAYETTEVILLE, ARK.]

The Stereochemistry of the Hydrogenation of Cycloölefins on Supported Palladium Catalysts[1,2]

BY SAMUEL SIEGEL AND GERARD V. SMITH[3]

RECEIVED MAY 5, 1960

The sterochemistry of the hydrogenation (1 atm.) of 1,2- (I) and 2,3-dimethylcyclohexene (II) and 2-methylmethylenecyclohexane (III) has been examined using palladium supported on alumina or charcoal as a catalyst and in a solvent (acetic acid or ethanol). The principal saturated product is *trans*-1,2-dimethylcyclohexane (IV), the more stable stereoisomer. Isomerization of the olefin competes with hydrogenation but does not occur in the absence of hydrogen. When the initial reactant is III (Pd-on-carbon), the relative concentrations of I and II remain far from the equilibrium ratio until III disappears. This indicates a competition between I, II and III for the catalytically active surface. Initially, III yields less of IV (61%) than does either I or II (73%). The results are interpreted in terms of the Horiuti–Polanyi mechanism in which the rate-controlling surface reaction is the conversion of the "half-hydrogenated states" to products.

In connection with our studies into the mechanism of the liquid phase hydrogenation of cycloölefins on noble metal catalysts,[4,5] we have noted as have others,[6] that palladium catalysts yield lower percentages of the less stable (*cis*) stereoisomer from 1,2- or 1,4-disubstituted cyclohexenes than does platinum.

Studies of a probably related phenomenon, the variation in the *cis/trans* ratio of olefins formed in the hydrogenation of disubstituted acetylenes as a function of the catalyst, have been numerous,[7,8] although except for relatively recent work[8,9] have suffered from inadequate analytical techniques. Also work on the simultaneous addition and exchange of deuterium with propylene on platinum and nickel catalysts suggests that the hydrogenation of an olefin occurs *via* similar mechanisms[10] on these catalysts although the distinctive features of the several catalytic systems are not sharply delineated.

We have now examined in some detail the behavior of 1,2-dimethylcyclohexene (I), 2,3-dimethylcyclohexene (II) and 2-methylmethylenecyclohexane (III) when treated in the liquid phase with hydrogen at near atmospheric pressures and ambient temperature, in contact with palladium supported upon alumina or charcoal to determine whether the observed stereochemistry would further clarify the mechanism of this reaction.

Experimental

The cyclolefins I, II and III and the solvents were those used in the preceding paper[5] and were at least 99% pure. The palladium catalysts (5% by weight) obtained from Baker and Company, Inc., of Newark, N. J., were supported on alumina, charcoal or calcium carbonate.

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[1] The support by a grant (NSF-G-4469) from the National Science Foundation is gratefully acknowledged.

[2] Presented at the Cleveland Meeting of the American Chemical Society, April, 1960.

[3] Taken in part from the doctoral dissertation of Gerard V. Smith, University of Arkansas, June, 1959.

[4] S. Siegel and M. Dunkel, "Advances in Catalysis," Vol. IX, edited by A. Farkas, Academic Press, Inc., New York, N. Y., 1957, p. 15.

[5] S. Siegel and G. V. Smith, THIS JOURNAL, **82**, 60872 (1960).

[6] A. S. Hussey, Department of Chemistry, Northwestern University, private communication.

[7] K. N. Campbell and B. K. Campbell, *Chem. Revs.*, **31**, 77 (1942).

[8] R. L. Burwell, Jr., *ibid.*, **57**, 895 (1957).

[9] R. L. Burwell, Jr., and W. M. Hamilton, Preprints, Division of Petroleum Chemistry, American Chemical Society, Vol. 4, No. 2, A-103 (1959).

[10] T. I. Taylor in "Catalysis," Vol. 5 (Edited by P. H. Emmett), Reinhold Publishing Corp., New York, N. Y., 1957, p. 344.

Most of the experiments were performed at 25° and a fixed pressure of one atmosphere as before. Approximately 0.02 g. of the supported catalyst, 10.0 ml. of the solvent, and 0.16 g. of the olefin were generally used in each experiment.

The reaction could be stopped conveniently when desired, and the olefins and the products isolated from the reaction mixture without fractionation and analyzed by gas-liquid partition chromatography.[5] The results are recorded in Tables I and II and Figs. 1, 2 and 3.

TABLE I

HYDROGENATIONS OVER 5% Pd ON ALUMINA, SOLVENT, ACETIC ACID (1 ATM.)

Substrate	Reduced, %	Saturates, % *trans*	*cis*	Dimethylcyclohexene, % 2,3-	1,2-	*o*-Xylene, %
1,2-	61.6	46.0	15.6	3,8	33.6	0.9
2,3-	61.8	47.3	14.5	5.3	32.9	.0
Exo-	53.9	42.9	16.4	5.4	35.3	.0

TABLE II

HYDROGENATION OF 2-METHYLMETHYLENECYCLOHEXANE[a] ON 5% Pd-ON-CHARCOAL, SOLVENT, ETHANOL (1 ATM.)

Expt.	Reduction, %	Composition, % *trans*	*cis*	*exo-*	2,3-	1,2-	2,3-/1,2-
78	8.4 ± 0.3	5.2 ± 0.1	3.2 ± 0.2	65.2 ± 0.1	15.9 ± 0.1	10.4 ± 0.1	1.52
77	12.1 ± .2	7.3 ± .0	4.8 ± .2	54.9 ± .2	19.4 ± .2	13.6 ± .2	1.43
74	21.5 ± .5	13.2 ± .2	8.3 ± .3	20.1 ± .2	32.8 ± .4	25.6 ± .2	1.28
80[b]	24.0 ± .5	13.0 ± .3	11.0 ± .2	53.8 ± .4	14.7 ± .3	7.5 ± .1	1.96
75	26.5 ± .3	16.9 ± .2	9.6 ± .1	6.8 ± .0	36.6 ± .7	30.1 ± .6	1.21
73	40.3 ± .8	27.0 ± .6	13.3 ± .2	0.0	16.5 ± .0	43.2 ± .5	0.38
76	53.0 ± .6	36.1 ± .4	16.9 ± .2	.0	5.9 ± .2	41.2 ± .8	.14
52[c]	53.9	42.9	29.9	.0	5.4	35.3	.15
79	64.9 ± .2	45.1 ± .1	19.8 ± .1	.0	3.5 ± .2	31.6 ± .1	.11

[a] The composition of the starting material was 99.0% of the *exo* and 1.0% 2,3-. [b] The solution contained 0.2 ml. of 8 *N* sodium hydroxide. [c] The catalyst was 5% palladium-on-alumina.

Equilibration of Olefins.—Solutions of the olefins (0.2 ml.) in glacial acetic acid (10 ml.) containing 0.2 g. of *p*-toluenesulfonic acid were maintained at 25° for 37 days.[11] Although equilibrium was apparently not attained in all three solutions, the results indicate the following equilibrium composition: I, 84.5 ± 3.5%; II, 15.5 ± 3.5%; III, 0.3 ± 0.3%.

Results

Palladium on Alumina.—Whether one starts with 1,2- or 2,3-dimethylcyclohexene, approximately the same mixture is obtained when the reduction is stopped at about 60% of completion (Table I). 2-Methylmethylenecyclohexane yields a similar result. A more detailed study of the 1,2-isomer (Fig. 1) shows that during hydrogenation it is isomerized rapidly to a mixture of the 1,2- and 2,3-dimethylcyclohexanes whose ratio is, within experimental error, the independently determined equilibrium value. A small amount (~ 1%) of *o*-xylene also accumulates. However, the saturated products, *cis*- and *trans*-1,2-dimethylcyclohexanes, are produced at a substantially constant ratio throughout the reduction. In the absence of hydrogen, the olefins do not isomerize on the catalyst.[12,13]

The initial rate of uptake of hydrogen by the isomeric olefins is III > II > I (Fig. 2). The rate of disappearance of hydrogen does not show a simple order with respect to the substrate. However, the shape of each curve is consistent with the observed rapid isomerization of the starting olefin to a mixture which is hydrogenated more slowly.

Palladium-on-Charcoal.—The reduction of 2-methylmethylenecyclohexane (III) on palladium supported on charcoal (Fig. 3) is particularly instructive (the solvent being ethanol). The concentration of III drops linearly with the amount of hydrogen absorbed up to about 25% of the reaction. *cis* and *trans* 1,2-dimethylcyclohexanes are produced as are the isomeric olefins, 2,3- and 1,2-dimethylcyclohexene. Again the saturated product consists mainly of the more stable isomer; however, it is the *less stable* of the two olefins which is formed in the larger amount. Although the ratio of the saturated isomers remains fairly constant during this period (39 ± 1% *cis*), the ratio of 2,3- to 1,2-dimethylcyclohexene drops steadily. Shortly beyond 30% reduction, the *exo* isomer is no longer detected and the 2,3-isomer passes its maximum concentration to disappear more rapidly than the 1,2- isomer. The composition of the mixture during the last 40% of the reaction is practically the same as that observed during the corresponding part of the reduction of 1,2-dimethylcyclohexene on palladium supported on alumina.

These data suggest that during the first portion of the reduction of 2-methylmethylenecyclohexane (III), both isomeric olefins (I and II) and the saturated products are formed from a common intermediate which is derived from III. Further, once the olefins I and II are produced they must compete with III for the effective surface of the catalyst; and it is apparent that the order of selectivity is III > II > I; III does not exclude II completely from the surface for the ratio of II/I decreases in direct proportion to the amount of III (or the amount of hydrogen) which has disappeared up to about 25% reaction. Likewise, II does not completely exclude I from the surface because a steady ratio of the two is reached well before reduction is complete. During the latter portion of the reduction, the ratio of *cis*- to *trans*-1,2-dimethylcyclohexane changes in the direction of yielding more of the more stable isomer (a change from 61% to 70% *trans*).

An experiment (80) in which a few drops of sodium hydroxide was added to the reaction mixture resulted in a slower reduction; and the ratio of *cis*- to *trans*-1,2-dimethylcyclohexanes increased (46% *cis*) as did the ratio of 2,3- to 1,2-dimethylcyclohexene (1.96). The effect of alkali apparently is to decrease those processes which lead to the equilibration of olefins or other intermediates relative to the hydrogenation process.

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[11] A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell and Z. Jacura, THIS JOURNAL, **81**, 3153 (1959).

[12] W. G. Young, R. L. Meir, J. Vinograd, H. Bollinger, L. Kaplan and S. L. Linden, *ibid.*, **69**, 2046 (1947).

[13] T. I. Taylor and V. H. Dibeler, *J. Phys. Chem.*, **55**, 1036 (1951).

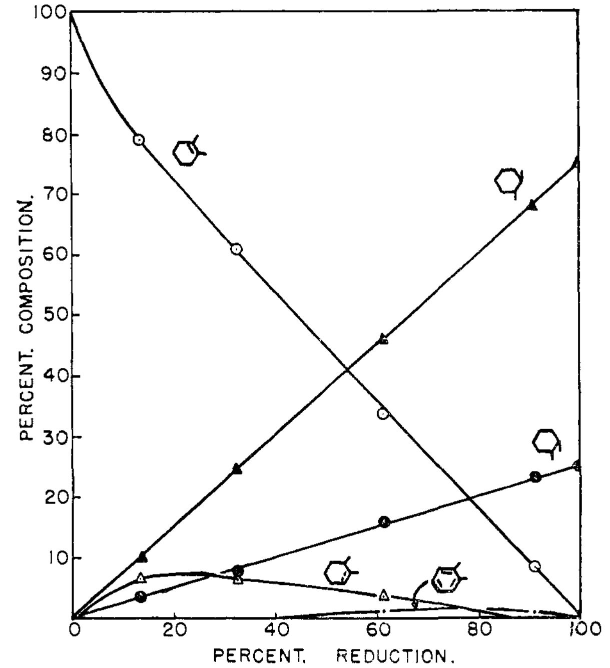

Fig. 1.—Hydrogenation of 1,2-dimethylcyclohexene on 5% Pd-on-alumina at 1.0 atm.

Discussion

The above results are consistent with the mechanism of hydrogenation proposed by Horiuti and Polanyi[14] which is represented for the compounds studied in Fig. 4. of the preceding paper.[5]

Reaction occurs on the surface of the catalyst between chemisorbed hydrogen and the adsorbed olefins (1,2-diadsorbed alkane)[15] or the "half-hydrogenated state" (monoadsorbed alkane). It is apparent that if the rate-controlling reaction upon the surface of the catalyst is the formation of the saturated products, then the preceding reactants and intermediates should tend to become equilibrated with one another. The extent of this approach to equilibrium, however, is a function of the rates of the pertinent reactions.

Conformational analysis may be used to predict the relative stabilities of the intermediates and, if the transition states for the postulated rate-limiting step resembles the preceding intermediates (the "half-hydrogenated states"), then the configuration of the main saturated isomer may be predicted also. Assuming that the larger the group the greater will be the difference in energy between an equatorial and axial position, yields the following sequence of stability: i > k >> f > d >> b > g and, consequently, if the intermediates approach their equilibrium distribution then the *trans* saturated product would be formed in major amount. The assignment of decreasing stabilities to primary > secondary > tertiary "half-hydrogenated states," is suggested also by the infrared spectral studies of Eischens.[16]

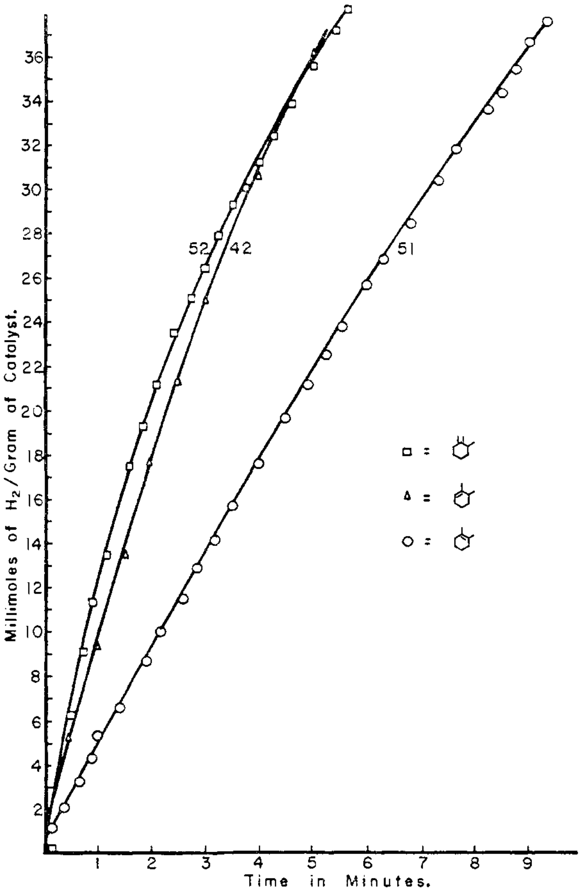

Fig. 2.—Rates of hydrogenation of the olefins on 5% Pd-on-alumina at 1.0 atm.

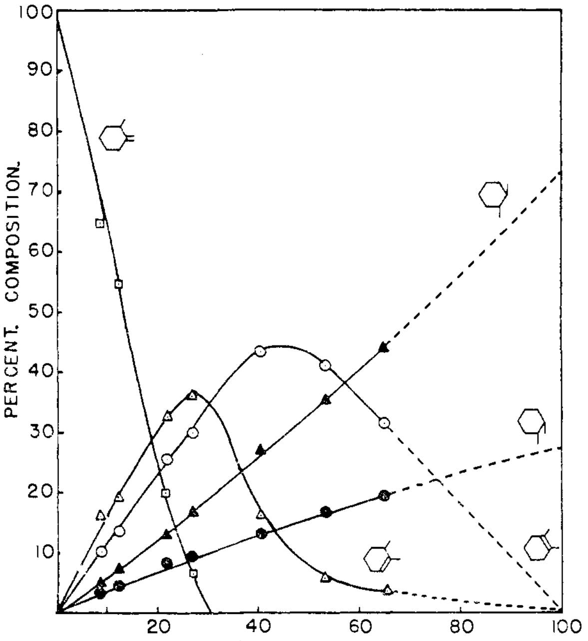

Fig. 3.—Hydrogenation of 2-methyl-1-methylenecyclohexane on 5% Pd(carbon) at 1.0 atm.

An equilibrium distribution of the "half-hydrogenated states" is approached but not attained at 1

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[14] I. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

[15] R. L. Burwell, Jr., B. K. S. Shim and H. C. Rowlinson, THIS JOURNAL, **79**, 5142 (1957).

[16] R. P. Eischens and W. A. Pliskin, "Advances in Catalysis," Vol. X, Academic Press, Inc., New York, N. Y., 1958, p. 1.

atmosphere of hydrogen because the several olefins yield somewhat different percentages of the *trans* isomer I (75), II (77) and III (61). As one would expect, increasing the pressure of hydrogen gives a result indicating a further displacement from equilibrium; accordingly 1,2-dimethylcyclohexene (I) yields 62% *trans* at 150 atmospheres of hydrogen on alumina. Conceivably, the fewer the steps required to go from one species to another, the more closely their ratio might approach the equilibrium value. Thus, when starting with the *exo*-olefin, equilibrium may be closely approached with respect to the species immediately derived from it before it is equilibrated with the intermediates derived directly from the isomeric olefins, thus accounting for the small difference in the ratio of *cis/trans* isomer on starting with I, II or III, respectively. Equilibrium among the diadsorbed species is probably reached more quickly and apparently the rate of their desorption under the conditions of the reaction is rapid. However, conformational analysis suggests that the diadsorbed species (a), which alone can yield 1,2-dimethylcyclohexene, is a higher energy intermediate than the other diadsorbed states represented. Consequently, when starting with III and under kinetic control, the reaction mainly follows the path leading to 2,3-dimethylcyclohexene *via* c or e until the *exo* isomer III disappears and no longer supplies e through g. The selectivity in reduction of the olefins suggests that the catalyst's surface is saturated with the intermediates; otherwise one olefin could not prevent another from reacting (as they apparently do), although separately the three olefins react at somewhat comparable rates. Although the kinetic study is incomplete, it indicates an approximate zero order dependence on the concentration of the substrate.

Relative to the behavior on platinum, palladium yields results which suggest that on it hydrogen abstraction reactions are faster than hydrogenation. Consequently, the isomerization of an olefin is readily observed when the latter is used. For example, a platinum catalyst at about one atmosphere of hydrogen yields no 2,3-dimethylcyclohexene (II) when 1,2-dimethylcyclohexene (I) is reduced, although it is posulated that almost all of I goes to II before becoming saturated.[5] Likewise some of I is formed when II is hydrogenated although the ratio is far from the equilibrium value.[5]

Catalyst Selectivity in the Hydrogenation of Acetylenes.—An explanation for the generally greater selectivity of palladium over platinum catalysts for the hydrogenation of acetylenes to olefins can be developed from the preceding discussion of the differences in the reaction of hydrogen with olefins on such catalysts.[17] The greater selectivity resides in the catalyst for which the rate-controlling step is the dissappearence of the "half-hydrogenated state" of the olefin. On palladium, this step is slow relative to the establishment of the olefin–adsorbed olefin (1,2-diadsorbed alkane) equilibrium. Consequently, the surface becomes covered with the most strongly adsorbed unsaturated species. Because acetylenes are held more tightly than olefins, a molecule of olefin once desorbed has little chance to return to the surface until all of the acetylene has been consumed. If a catalyst such as platinum is employed, there is less opportunity for the intermediates to become desorbed since the rate-limiting reaction is the *formation* of the "half-hydrogenated" state[5] and, consequently, a mixture of saturated and unsaturated compounds is produced before all of the acetylene has been transformed. Although some palladium catalysts lack the high selectivity in the hydrogenation of acetylene to olefins referred to above, these are generally porous solids[17] and the reduced selectivity may be attributed to the possibility that the diffusion of the acetylene into the pores is the limiting factor.[18] Such catalysts frequently improve with use[9]; in effect, the catalytically active surface which is deep in the pores is deactivated, perhaps through the formation of high polymers which cannot be easily desorbed.

(17) G. C. Bond, "Catalysis," Vol. 3, Edited by P. H. Emmett, Reinhold Publishing Corp., New York, N. Y., 1955, p. 143.

(18) A. Wheeler, "Advances in Catalysis," Vol. III, Academic Press, Inc., New York, N. Y., 1951, pp. 317–322.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY, EVANSTON, ILL.]

The Hydrogenation of Cyclohexenes over Platinum Oxide

BY JAMES-FREDERICK SAUVAGE,[1] ROBERT H. BAKER AND ALLEN S. HUSSEY

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The hydrogenation of nine 1,4-disubstituted cyclohexenes, 1,3-dimethylcyclohexene and $\Delta^{9,10}$-octalin in acetic acid over platinum oxide at 1 atmosphere and room temperature has been carried out. Only one of the compounds studied has been found to show appreciable isomerization in the course of hydrogenation under these conditions. The *cis–trans* isomer compositions of the product mixtures have been determined. An explanation of the stereochemical results is offered.

The present status of knowledge concerning the catalytic addition of hydrogen to carbon–carbon unsaturation can be summarized by the mechanism of steps 1-4, which paraphrases a theory of long standing.[2]

Steps 1 and 2 represent the chemisorption of hydrogen and of alkene on the catalyst surface by reversible processes. The heat liberated in step 2 may be as much as twice that of step 1.[3] Steps 3 and 4 represent the consecutive addition of hydrogen atoms, each also reversible. The reversal of

(1) Abstracted in part from the Ph.D. Thesis of J. F. S., September, 1959; Monsanto Co. Fellow, 1955–1957; United States Rubber Co. Fellow, 1957–1958.

(2) I. Horiuti and M. Polyani, *Trans. Faraday Soc.*, **30**, 1164 (1934).

(3) For a discussion of these values see D. D. Eley in "Catalysis," Vol. III, P. H. Emmett, Editor, Reinhold Publishing Corp., New York, N. Y., 1955, pp. 59–63.