one to assign the exchange of adamantane which exchanges only one hydrogen atom per period of adsorption (see paper II)? We do not know how the five types of sites contribute to this exchange. One might find out by detailed comparison of the rate of exchange of adamantane with the rates of the five types of cyclopentane exchange on the catalysts of Figures 1 and 2.

Finally, what could one say about the contribution of these five sites to the hydrogenation of ethylene? Only that if all of these five sites contribute (and there may be *more* than five) the details of the resulting composite reaction may be rather complicated. For example, an attempt to interpret the over-all rate data in terms of Langmuir–Hinshelwood kinetics might be very misleading.

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The Mechanism of the Isotopic Exchange between Deuterium and Cycloalkanes on Palladium Catalysts

Klaus Schrage and Robert L. Burwell, Jr.

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois. *Received December 9, 1965*

Abstract: In isotopic exchange between deuterium and bicyclo[3.3.1]nonane on palladium-on-alumina catalysts at about 60°, the eight hydrogen atoms which form the set which can be connected by *cis*-eclipsed conformations largely exchange as a unit. In addition, d_{10} and d_{12} appear in the initial products in substantial amounts but d_9 and d_{11} only in very small amounts. The large yield of d_8 supports the view that the fundamental exchange mechanism involves alternation between monoadsorbed and eclipsed diadsorbed alkane. The additional exchange of the second set of hydrogen atoms in cyclopentanes and cyclohexanes must involve separate sets of sites. Some form of the π-allyl mechanism is consistent with the results including formation of bicyclononane-d_{10} and -d_{12}. Also consistent is some form of a roll-over mechanism in which an eclipsed diadsorbed species rolls over *via* a species containing five-coordinate carbon atoms which are bonded to two different surface sites. The last process can also provide a mechanism for formation of cyclopentane-d_8. Exchange of cyclohexane contrasts with that of cyclopentane: highly exchanged species are formed in much lower concentrations; increasing partial pressure of deuterium leads to marked reduction in the relative yield of extensively exchanged cyclohexane. This appears to result from the readier formation in cyclopentane *vs.* cyclohexane of an eclipsed diadsorbed species and of whatever intermediate is involved in exchanging both sets of hydrogen atoms in cyclopentane and cyclohexane.

It has long been evident that reactions between hydrocarbon and hydrogen on metals of group VIII proceed *via* surface organometallic intermediates of which many are needed for the varied reactions of this class.[1] The original Horiuti–Polanyi mechanism[2] for olefin hydrogenation, one of the earliest proposals to involve specific surface organometallic species, is illustrated in Figure 1 for cyclopentene. It is now considered that all of the steps are potentially reversible and that the diadsorbed species must be in the eclipsed conformation.[3]

If the rate ratio r_{-2}/r_3 is large, the resulting alternation between mono- and diadsorbed cyclopentane leads to eventual desorption of $C_5H_5D_5$ in which all five hydrogen atoms on one side of the ring have exchanged as is observed on several metals of group VIII.[3–5] The two sets of hydrogen atoms on cyclopentane are equivalent but those on methylcyclopentane are not. Figure 2 shows that alternation between mono- and diadsorbed methylcyclopentane would exchange four hydrogen atoms, the "h set," if initial adsorption occurs in the h set (*i.e.*, with replacement of one h atom by a surface site), but eight hydrogen atoms can exchange, the "H set," if initial adsorption occurs in the H set. Thus, the methyl group exchanges with the hydrogen atoms *trans* to it. These predictions accord with observations.[2,3]

On nickel and palladium at above 100°[3–5] processes become dominant which exchange all hydrogen atoms in cyclopentane and which are associated with racemization of optically active alkanes[3] and epimerization in such compounds as 1,2-dimethylcyclopentane.[6] Earlier suggestions as to mechanism involved an additional and symmetric intermediate (1,1-diadsorbed cyclopentane[4] or 1-monoadsorbed cyclopentene[3]) which served to interconvert adsorption in the H- and h-sets and which, therefore, led to complete exchange. The monoadsorbed cyclopentene had the advantage of also giving racemization and epimerization.

Alternatively and more recently, two additional intermediates have been proposed, a π-olefin complex and a π-allyl one.[7] Alternation between the two is

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(1) R. L. Burwell, Jr., and J. B. Peri, *Ann. Rev. Phys. Chem.*, **15**, 141 (1964).

(2) G. C. Bond, "Catalysis by Metals," Academic Press Inc., London, 1962.

(3) R. L. Burwell, Jr., B. K. C. Shim, and H. C. Rowlinson, *J. Am. Chem. Soc.*, **79**, 5142 (1957).

(4) J. R. Anderson and C. Kemball, *Proc. Roy. Soc.* (London), **A226**, 472 (1954).

(5) K. Schrage and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **88**, 4549 (1966). This is considered paper I of this series.

(6) R. L. Burwell, Jr., and K. Schrage, *Discussions Faraday Soc.*, in press.

(7) F. C. Gault, J. J. Rooney, and C. Kemball, *J. Catalysis*, **1**, 255 (1962).

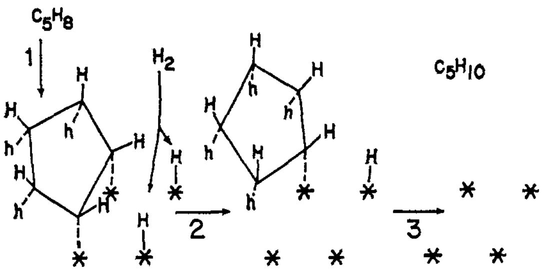

Figure 1. Horiuti–Polanyi mechanism as exemplified by cyclopentene. We shall consider all reactions as reversible.

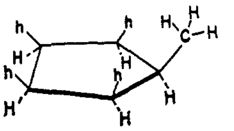

Figure 2. Identity of the two sets of hydrogen atoms in methylcyclopentane.

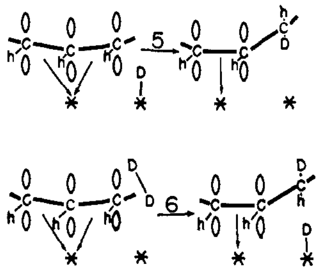

Figure 3. The π-allyl–π-olefin mechanism for two-set exchange. All reactions are considered reversible.

assumed to occur by two different elementary steps as shown in Figure 3 such that 6 followed by −5, or 5 by −6, would exchange the h set of hydrogen atoms, the one away from the surface. Coupled with the reactions of Figure 1, these intermediates lead to C_5D_{10} and, with appropriate reactants, to racemization and epimerization.

Still more recently, two groups of workers have proposed that olefin π-bonded to a single metal atom replaces eclipsed diadsorbed alkane in Figure 1.[8,9]

In the present paper, we attempt some elucidation of the mechanism of the isotopic exchange between alkanes and hydrocarbons on palladium catalysts in the light of the detailed characterization of these processes reported in paper I and in conjunction with results of isotopic exchange of 1,2-dimethylcyclopentane[6] and of cyclohexane, bicyclo[3.3.1]nonane, and adamantane reported in the present paper. The results with these hydrocarbons bear particularly upon whether eclipsed diadsorbed alkane or π-bonded olefin is appropriate in Figure 1 and upon the nature of the process leading to complete exchange and to epimerization.[10]

Experimental Section

Materials. The catalysts employed have been described in paper I. Cyclohexane Phillips Pure Grade, was purified by gas chromatography. 3,3-Dimethylpentane was prepared by hydrogenation of 3,3-dimethylpentene.[11]

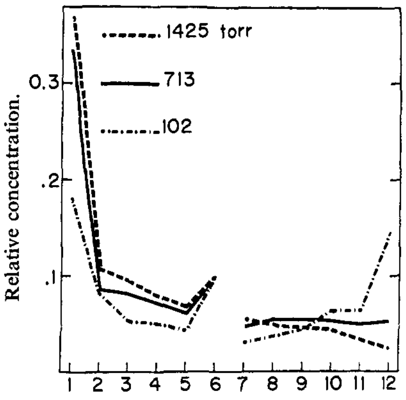

Figure 4. Effect of partial pressure of deuterium upon the isotopic exchange between cyclohexane and deuterium at 40° on catalyst V. The data are normalized to 0.1 at D_6. The partial pressure of cyclohexane was 38 torr. The partial pressure of hydrocarbon, total per cent exchange, and flow rate of hydrocarbon were: run 121, 1425 torr, 1.48%, 1.47 mmoles/hr; run 117, 713 torr, 1.27%, 2.67 mmoles/hr; run 120, 102 torr, 1.42%, 7.13 mmoles/hr.

Bicyclo[3.3.1]nonane was prepared from the ethylene ketal of bicyclo[3.3.1]non-2-en-9-one.[12] The ketal was converted to the ethylene thioketal[13] which was hydrogenated and desulfurized by Raney nickel in refluxing methanol. The bicyclononane was precipitated from its solution in methanol by addition of water, extracted into pentane, and isolated by distilling the pentane. It was recrystallized from methanol, mp 141.5–144° (sealed tube).[14] Gas chromatography indicated the presence of trace amounts of five impurities summing to less than 0.1%.

We are indebted to Dr. J. A. Marshall and Mr. C. J. V. Scanio for supplying us with the starting ketal and assistance in its conversion to bicyclononane.

Adamantane, Aldrich Chemical Co., contained four impurities summing to less than 0.2%.

Isotopic Exchange Reactions. Technics were described in paper I.[5] Mixtures of the vapor of solid hydrocarbons in deuterium were prepared by passing deuterium through a U-tube containing loosely packed hydrocarbon. A considerable surface of the hydrocarbon was exposed. However, we did not determine the actual degree of saturation.

Table I presents isotopic distribution patterns for the exchange of adamantane and bicyclo[3.3.1]nonane on catalyst VII. Because of some uncertainty as to their exact partial pressures we have not corrected these runs for isotopic dilution (see paper I). However, correction would be slight. Other runs in this paper have been corrected.

Figure 4 shows normalized isotopic exchange patterns of cyclohexane on catalyst V at 40° at three partial pressures of deuterium.

Discussion

Eclipsed Diadsorbed Alkane *vs.* π Complex. There is clearly some process which exchanges all or most of one set of hydrogen atoms, the h or H atoms in $C_5H_5h_5$, in $C_6H_8h_4$, etc., using the terminology of Figure 2. That this process involves alternation between monoadsorbed and some kind of diadsorbed species is supported by results with a number of hydrocarbons.[2] In particular, the exchange pattern of 3,3-dimethylpentane looks like the D_1–D_5 part of cyclopentane[15]

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[8] J. J. Rooney and G. Webb, *J. Catalysis*, **3**, 488 (1964).

[9] G. C. Bond and P. B. Wells, *Advan. Catalysis*, **15**, 91 (1964).

[10] Some of the results with the polycyclic hydrocarbons have been the subject of a preliminary communication: R. L. Burwell, Jr., and K. Schrage, *J. Am. Chem. Soc.*, **87**, 5253 (1965).

[11] R. Ciola and R. L. Burwell, Jr., *J. Org. Chem.*, **23**, 1063 (1958).

[12] C. S. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964).

[13] L. F. Fieser, *J. Am. Chem. Soc.*, **76**, 1945 (1954).

[14] The literature reports 143°: E. Buchta and S. Billenstein, *Naturwiss.*, **51**, 383 (1964).

[15] Exchange of 3,3-dimethylpentane, P_{D_2} = 650 torr, on catalyst V at 60°, gave D_1, 0.11; D_2, 0.06; D_3, 0.02; D_4, 0.05; D_5, 0.19; D_6 *et seq.*, 0.00.

Table I. Isotopic Distribution Patterns

	Adamantane		Bicyclo[3.3.1]nonane	
Run no.	VII 134		VII 137	VII 138
Temp, °C	60		50	70
D_2 flow[a]	48.5		39	158
P_{HC}, torr[b]	5		8	8
P_{D_2}, torr[b]	745		752	752
D_0, %	61.16	61.43[c]	98.09	98.38
D_1, %	31.21	30.40[c]	0.54	0.65
D_2, %	6.75	7.05[c]	0.11	0.055
D_3, %	0.72	1.02[c]	0.20	0.16
D_4, %	0.08	0.10[c]	0.105	0.10
D_5, %	0.03	0.01[c]	0.12	0.135
D_6, %	0.03	0.00[c]	0.08	0.095
D_7, %	0.00	0.00[c]	0.08	0.12
D_8, %			0.29	0.475
D_9, %			0.035	0.06
D_{10}, %			0.225	0.49
D_{11}, %			0.01	0.01
D_{12}, %			0.09	0.27
D_{13}, %			0.000	0.000

[a] Deuterium flow in millimoles per hour. [b] Partial pressures of deuterium and hydrocarbon in torr. [c] Binomial distribution for $C_{10}H_{16}$ containing an average of 0.48 deuterium atom and 16 exchangeable hydrogen atoms.

which indicates that the process can occur in a two-carbon chain. It cannot occur on an isolated carbon atom, for example methane or neopentane.[2]

The actual geometric difference between eclipsed diadsorbed alkane, A, and the newly proposed π-complexed olefin, B, is not really very large. In essence, merely bending back the bonds attached to the double bond will convert B into A. Thus, A and B make the same predictions for the number of hydrogen atoms in each set for cyclopentane, methylcyclopentane, and most other molecules. Are there, indeed, molecules for which A and B have different consequences?

The proposers of the π-complex form have not considered one set of experimental results which might have seemed in conflict with it. Cyclooctane on palladium on alumina at 60–80° gives large yields of perdeuteriocycloalkane, very low yields in the vicinity of half-deuteration, and no sign of a break between half-deuteration and half plus one.[3] We interpreted this as resulting from the possibility of forming *trans*-eclipsed diadsorbed cycloalkane with larger rings as well as the usual *cis*-eclipsed. The *trans* form interconnects the H set and the h set and permits alternation between mono- and diadsorbed to exchange both sides of the ring. The π-complex mechanism requires π-complexed *trans*-cyclooctene, a species which would seem far too strained, to be very probable. One can avoid this objection only by arguing that the two-set exchange process (the d_{10} process of cyclopentane, paper I) is for some reason so overwhelmingly favored for cyclooctane that the one-set process is obscured.

Another class of molecules can discriminate between A and B. Bredt's rule forbids the formation of a double bond at a bridgehead but eclipsed conformations are also forbidden. As the ring size enlarges, these rules are relaxed but the prohibition against eclipsed conformations relaxes first.[16] In adamantane ($C_{10}H_{16}$), Figure 5a, all vicinal pairs of hydrogen atoms are rigidly held in staggered conformations. Any adamantane would be of very high energy. Thus, adamantane should exchange only one hydrogen atom per period of adsorption, a prediction[3] substantiated by the accord to a binomial distribution in run 134 of Table I.[17] Let us now, in imagination, hydrogenolyze away one of the methylene groups to get bicyclo[3.3.1]nonane, Figure 5b. The larger rings now permit eclipsed conformations at the bridgehead although a double bond at the bridgehead would still be rather high in energy, too high when π-complexed to serve as an intermediate. Figure 5b shows bicyclononane with one cyclohexane ring in the chair, one in the boat form. Alternatively, one may consider it as one of the more favorable conformations of cyclooctane[18] bridged by methylene. It corresponds to *trans*-eclipsed cyclooctane. Eclipsed 2,3-diadsorbed is also possible. Therefore the eight atoms of the H set in Figure 5b can be exchanged by the classical scheme of Figure 1. A π-complexed intermediate with the geometry of an olefin can lead to the exchange of the three H atoms at 2, 3, and 4 or 6, 7, and 8, but this intermediate cannot lead to exchange of the bridgehead hydrogen atoms and, therefore, it cannot interconnect exchange in the two trimethylene groups. Further, two-set exchange cannot lead out of one trimethylene group *via* a process involving π-adsorbed allyl at atoms 2, 1, and 8 since this would also be a high-energy form. Thus, eclipsed diadsorbed alkane, A, gives a maximum at D_8 as observed; π-complexed olefin, B, cannot.

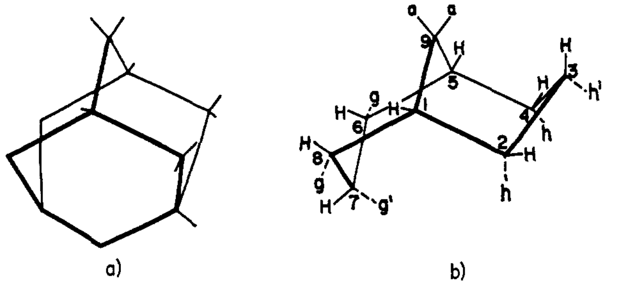

Figure 5. (a) Adamantane. (b) Bicyclo[3.3.1]nonane. Hydrogen atoms are classified into four sets, H, h, g, and a.

This argument refers to molecular geometry and not to the details of bonding. We conclude only that the diadsorbed species has a geometry nearer that of eclipsed alkane than that of olefin. At present, there seems to be no justification for introducing a π-complexed olefin into this particular reaction, although, of course, there might be some contribution of olefin to a resonance hybrid. $\Delta_{1,2}$-Bicyclononene, like *trans*-cycloctene, may be an isolable compound. But even allowing for the somewhat greater stability of π complexes of strained olefins, one could hardly expect that the energy differences between monoadsorbed cycloalkane and π-complexed olefin would be about the same for cyclopentane and bicyclononane.

Arguments based upon molecular analogies[8,9] are often useful but they involve the disadvantage in the present instance that known molecular π-complexed olefins are mononuclear but that surfaces are poly-

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(16) See, for example, E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., 1962, p 301.

(17) For another example of this and the computational procedure, see G. Pass, A. B. Littlewood, and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **82**, 6281 (1960).

(18) Conformation II in K. B. Wiberg, *ibid.*, **87**, 1070 (1965). However, in the solid state, both cyclohexane rings are almost surely in the chair form: M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, **47**, 695 (1964); see also, R. Lygo, J. McKenna, and I. O. Sutherland, *Chem. Commun.*, 356 (1965).

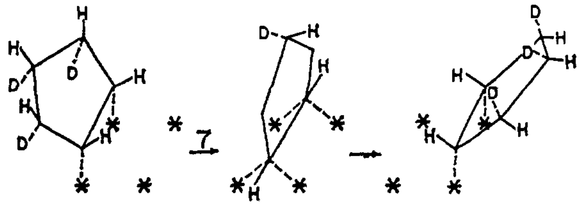

Figure 6. The roll-over mechanism.

nuclear. In our view, the adsorbed species are likely to be bonded to several surface atoms in the way in which carbon and nitrogen are bonded in metallic carbides and nitrides.

Mechanism of d_8 Exchange. The exchange process leading to cyclopentane-d_8 and to 1,1-dimethylcyclopentane-d_6 probably proceeds on separate sites as reported in paper I. We need a process of rather low probability which exchanges three additional hydrogen atoms. A process of high probability would occur several times during one period of adsorption and give d_{10}. We suggest that cyclopentane-d_8 is formed on a section of surface with a high probability of forming d_5 and a small probability of the roll-over process shown in Figure 6. The transition state shown in the middle is presumed to involve coordination at the adsorbed carbon atoms which is approximately trigonal bipyramidal. The sequence—exchange by the one-set process, roll-over, exchange by the one-set process, desorption—gives cyclopentane-d_8.

Mechanism of Two-Set Exchange. For simplicity, consider first just the application to cyclopentane at temperatures at which $D_5 \simeq D_{10}$. In addition to the one-set process which gives mainly d_5, there must be one or more of the following.

A. An additional and symmetric intermediate can form on the same set of sites used for one-set exchange. It can react to form species adsorbed in the H set or in the h set, and thus it permits adsorption in one set to shift to adsorption in the other set.

B. The switch from adsorbed forms characteristic of one-set exchange to those which lead to two-set exchange occurs *via* migration to a *different set of sites.*

C. The two-set exchange process occurs independently of one set on a *different set of sites.*

The evidence of paper I that one- and two-set exchange occur on different sets of sites constitutes an objection to A. In addition, there is the following objection. Any symmetric intermediate in A could not be missing hydrogen atoms from the as yet unexchanged set. Suppose that 1,1-diadsorbed cyclopentane is the symmetric intermediate. It will first form as $C_5(H_4*)(d_4*)$ which, in reverting to monoadsorbed cyclopentane, forms $C_5(H_4*)(d_5)$ and $C_5(H_4D)(d_4*)$ with equal probability. Thus, under conditions in which the yield in d_5 is to remain substantial, that in d_6 must also be substantial, but almost none is observed. Process A could not involve 1,1-diadsorbed cyclopentane, 1-monoadsorbed cyclopentene, or any other species in which between one and four hydrogen atoms have been removed from the as yet unexchanged set. Nor can hydrogen atoms be missing from the exchanged set as exemplified by the roll-over mechanism of the previous set. In fact, the symmetric intermediate could not be derived from cyclopentane by *dissociative* adsorption.

However, all three intermediates could operate in processes B and C in which case they will form and re-form many times during one period of adsorption rather than just once or twice as would be required in A to retain a large value of D_5. There are also a number of other possible mechanisms. We clearly need other data to distinguish among these possibilities.

A study of the isotopic exchange and accompanying epimerization of *cis-* and *trans-*1,2-dimethylcyclopentanes[6] establishes that both form the same highly exchanged intermediate which desorbs as highly exchanged *cis-* and *trans-*1,2-dimethylcyclopentane in the ratio of 1:4.

The multiset exchange process in bicyclononane is of considerable mechanistic interest. What are the two pairs of hydrogen atoms which exchange to give d_{10} and d_{12} (Table I)? From the results with adamantane one would expect atoms a at position 9 not to exchange in conjunction with any others barring the intrusion of some transannular process. If the two pairs which do exchange are identical pairs, as seems likely, they are either (i) h,h and g,g or (ii) h(2),g(8) and h(4),g(6). On palladium, as expected, 1,1,3,3-tetramethylcyclohexane exchanges three atoms by one-set exchange. Additionally, at lower temperatures, it exchanges two more for a total of five.[19] Bicyclononane also has trimethylene units. We suggest that the pairs which give d_{10} and d_{12} are h,h and g,g.

In the one-set exchange process leading to bicyclononane-d_8, species which are eclipsed and diadsorbed in the H set appear to be intermediates as we have shown. The large ratio D_8/D_3 requires formation of bridgehead diadsorbed bicyclononane to be fast relative to desorption.

In multiset exchange, D_{10} is large *vs.* D_9 and D_{11}. Thus, in exchange of the h and g sets, the exchange process is largely contained in one trimethylene unit but exchange is not contained in exchange of the H set. Therefore, if multiset exchange is type C (formation of D_{10} and D_{12} directly from gas phase reactant) (a) the finite ratio D_{10}/D_{12} requires D_8/D_{10} to be finite. Further, eclipsed diadsorbed in the H set can be an intermediate only (b) if both h atoms exchange without intermediate formation of eclipsed diadsorbed in the H set and if (c) the possibility of exchange of h′ is avoided.

If multiset exchange is type B, restriction b can be dropped for the sites to which migration occurs after one-set exchange. The sites being different and H set exchange already accomplished, formation of bridgehead diadsorbed can be assumed relatively less probable than on one-set sites. Or, two-set sites could exist as isolated small units and transfer from one trimethylene unit to the other could require return to one-set sites.

In exchange *via* alternation between monoadsorbed and eclipsed diadsorbed cyclopentane (Figure 1), the degree to which complete exchange of one set of hydrogen atom occurs is determined by the ratio

$$r_{-2}/r_3 = \frac{k_{-2}/k_3}{(KP_{\mathrm{H_2}})^{1/2} + KP_{\mathrm{H_2}} + k_{-3}P_{\mathrm{RH}}/k_3} \qquad (1)$$

using Langmuir–Hinshelwood kinetics and assuming that the fraction of surface covered by diadsorbed alkane is small. The quantities are those defined for r_{-3} in eq 5 of paper I. Equation 5 is applicable here.[20] The rate

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(19) J. J. Rooney, *J. Catalysis*, **2**, 53 (1963).

ratio will decrease with increase in pressure of deuterium, *i.e.*, the fraction of molecules in which one set of hydrogen atoms is completely exchanged will decrease with increase in partial pressure of deuterium.

Let us assume that two-set exchange proceeds by initial adsorption as monoadsorbed followed by conversion to other species in which one or more additional hydrogen atoms are removed. Then, an equation of the general form of eq 1 will determine the fraction of molecules in which two sets of hydrogen atoms are completely exchanged.

In fact, since the perdeuterio fraction of cyclopentane and substituted cyclopentanes is large, the rate ratio must be very large, so large that the effect of pressure of deuterium upon the distribution of product within the two-set exchange process is not evident. Presumably at high enough partial pressures of deuterium, the perdeuterio fraction would visibly decline. One-set exchange exhibits the same properties. Quite probably, at least one of the two processes which give low degrees of exchange differs from one-set exchange mainly in having a much smaller ratio, k_{-2}/k_3 (see paper I).

As shown in Figure 4, the behavior of cyclohexane is different. Two-set exchange gives a smeared distribution and a much smaller yield of perdeuterio than with cyclopentane. Further, the partial pressure of deuterium considerably influences the distribution. Perdeuterio is a maximum at 100 torr of deuterium but a minimum at 1410 torr. Cycloheptane and cyclooctane resemble cyclopentane in giving a very large yield of perdeuterio.[3]

We suggest that the different behavior of cyclohexane has the following origin. The initial process in all cases is reaction -3, dissociative adsorption of cycloalkane to form monoadsorbed cycloalkane. In one-set exchange, eclipsed diadsorbed cyclopentane will be formed more readily than eclipsed diadsorbed cyclohexane because cyclohexane must go into some form of a boat conformation whereas the bonds in cyclopentane are nearly eclipsed initially. Eclipsed conformations are also easier in cyclooctane and cycloheptane.[18] We must conclude that those intermediates in two-set exchange which form from monoadsorbed are also of a type easier to form with cyclopentane, for example, π-complexed olefin or eclipsed diadsorbed.[21]

Thus, any mechanism should couple epimerization (or racemization where appropriate) with multiset exchange, it should involve a difficulty in transferring adsorption from one trimethylene unit in bicyclononane to the other, and it should lead to the exchange of only five of six hydrogen atoms in trimethylene units of this type. As shown for 1,1-dimethylcyclopentane in paper I, all hydrogen atoms in tetramethylene units can exchange whereas no two-set exchange occurs in rings with isolated ethylene units as in bicyclo[2.2.1]heptane.[3,6] Finally, the extra intermediate or intermediates responsible for two-set exchange are of a type more readily formed with cyclopentane than with cyclohexane.

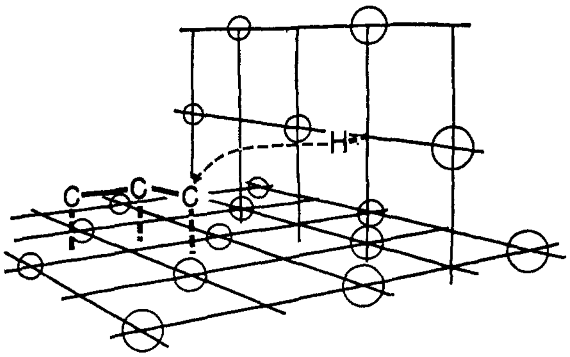

Figure 7. The π-allyl mechanism at a step.

Alternation between π-complexed olefin and π-allyl formally satisfies these requirements. As may be seen in Figure 3, processes 5 and 6 can never exchange the central h atom in an isolated trimethylene unit.[19] Further, if two of the h atoms are substituted by methyl, epimerization will accompany two-set exchange. We do not see how to achieve both of these requirements with analogs of 1,1-diadsorbed cyclopentane and 1-monoadsorbed cyclopentene.

The D–D bond in deuterium, 0.74 A, is short relative to the other bonds, 1.1 for C–H, 2.1 for C–*, and 1.7 for H–*.[22] It would appear that the minimum separation of the hydrogen nuclei in the transition state of reaction 6 is about 1.5 A or larger, if one is to avoid the van der Waals radii of other atoms. It is, therefore, not clear that the hydrogen atoms can be substantially bonded during the doubling of the separation occasioned by reaction 6 and the occurrence of a low-energy transition state for reaction 6 may be difficult. The possible difficulty is avoided if the reaction occurs at a step on the surface as shown in Figure 7. A screw dislocation might serve as such a site and the reaction which adds a deuterium atom above the plane of the cyclopentane might be either reaction 6 or, as shown in Figure 7, another reaction 5 from the other face.

The roll-over mechanism of the section, Mechanism of d_8-Exchange, can also be adapted to two-set exchange. One needs to assume that migration occurs from a set of sites giving very extensive one-set exchange[23] to sites in which the probability of roll-over, reaction 7 in Figure 6, is large with respect to desorption of hydrocarbon and in which 2,3-diadsorbed bicyclononane is several times more probable then 1,2-diadsorbed. The pairs of sites which are employed might be those on opposite sides of the troughs in the (110) faces of fcc metals.[24] This process would give complete exchange of cyclopentane, epimerization of dimethylcyclopentanes, and an upper limit of d_5 in an isolated trimethylene unit. The last result is shown below. The species at the

$$\begin{bmatrix} \mathrm{D} & \mathrm{h} \\ * & \mathrm{h} \\ * & \mathrm{h} \end{bmatrix} \xrightarrow{\text{roll-over}} \begin{bmatrix} \mathrm{D} & \mathrm{h} \\ \mathrm{h} & * \\ \mathrm{h} & * \end{bmatrix} \xrightarrow{2,\,3,\,2} \begin{bmatrix} \mathrm{D} & * \\ \mathrm{h} & * \\ \mathrm{h} & \mathrm{d} \end{bmatrix}$$

$$\begin{bmatrix} \mathrm{D} & * \\ \mathrm{h} & * \\ \mathrm{h} & \mathrm{d} \end{bmatrix} \xrightarrow{\text{roll-over}} \begin{bmatrix} * & \mathrm{D} \\ * & \mathrm{h} \\ \mathrm{h} & \mathrm{d} \end{bmatrix} \xrightarrow{2,\,3,\,2} \begin{bmatrix} \mathrm{D} & \mathrm{D} \\ * & \mathrm{h} \\ * & \mathrm{d} \end{bmatrix}$$

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(20) We do not wish to stress too much these approximate solutions to an oversimplified model but they should show the general nature of the dependence upon partial pressures of deuterium and hydrocarbon.

(21) And perhaps π-allyl although no definitive data establish this. Since the heats of hydrogenation of both cyclohexene and 1,3-cyclohexadiene exceed those of the corresponding cyclopentenes (G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, **58**, 146 (1936)), C_5H_7 with three sp^2 carbon atoms is probably also more stable with respect to monoadsorbed cycloalkane.

(22) S. J. LaPlaca and J. A. Ibers, *J. Am. Chem. Soc.*, **85**, 3501 (1963).

(23) This is needed in all of these mechanisms to get the large ratios, D_{10}/D_9 and D_{12}/D_{11}, in bicyclononane.

(24) For the geometry of these sites and that of surfaces with larger troughs obtained by rearrangements of (110) faces; see J. F. Nicholas, *J. Phys. Chem. Solids*, **24**, 1279 (1963)

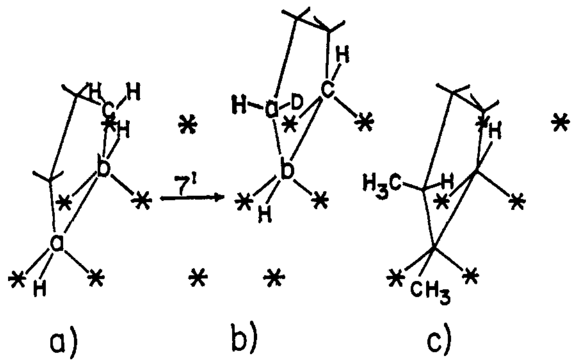

Figure 8. Alternative form of roll-over mechanism.

upper left is the starting form. Roll-over followed by reactions 2, 3, and 2 of Figure 1 gives the form at the upper right. Continuation of these reactions can never exchange the h atoms on the central carbon atom. The necessity for two free sites in the roll-over will give inhibition by deuterium.

In a conceivable if very speculative variant of this, what is represented as a transition state in Figure 6 might be an intermediate. Reaction of a form adsorbed at carbon atoms a and b to the form adsorbed at b and c, Figures 8a and 8b, would explain two-set exchange and d_5 exchange in a trimethylene unit. Further, the process could provide epimerization *via* the adsorbed species of Figure 8c which could revert to either epimer. The transition state of Figure 6, the species of Figure 8, and those of Figure 3 involve a plane parallel to the surface of the catalyst in which some of the atoms are bonded and some nonbonded. In Figure 8a, for example, the bonded carbon atoms a and b and two nonbonded hydrogen atoms are in a line parallel to the surface. This poses problems which are difficult to evaluate on the basis of our present knowledge of surface structure.[25]

Thus, of the several types of exchange processes which occur on palladium catalysts, that for extensive one-set exchange looks reasonably well outlined: alternation between monoadsorbed alkane and eclipsed diadsorbed is fast compared to desorption of monoadsorbed. One of the processes giving low degrees of exchange may well be similar but involves sites on which the monoadsorbed is relatively more likely to desorb rather than to revert to diadsorbed. We cannot rigorously choose among two types of processes for the two-set exchange process, a π-allyl process and a roll-over process. We shall need isotopic exchange experiments with molecules which can discriminate for or against allyl. In fact, available data on the isotopic exchange patterns of cycloalkanes might be able to discriminate if we had independent evidence as to the relative stability of π complexes for cyclohexane *vs.* cyclopentane and cycloheptane. However, really well-worked-out mechanisms must await more information about the detailed nature of surfaces and the nature of bonding to surface sites than we now possess.

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(25) See also ref 6.