

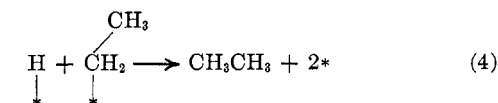
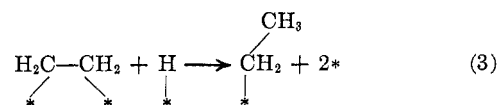
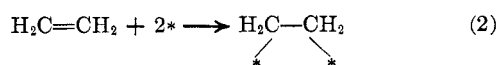
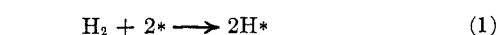
## Deuterium as a Tracer in Reactions of Hydrocarbons on Metallic Catalysts

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In 1934, Horiuti and Polanyi proposed the mechanism given by eq 1-4 for the hydrogenation of ethylene on the surface of metallic nickel. The asterisks represent



what we might now call coordinatively unsaturated surface sites. As modified and elaborated since 1934, the mechanism appears to give a good representation of many aspects of catalytic hydrogenation and related reactions on metals of group VIII, particularly nickel, platinum, palladium, and rhodium.

Until relatively recently, the absence of molecular analogies to the surface intermediates of reactions 1, 2, and 3 gave a somewhat *ad hoc* appearance to the mechanism. However, the spate of discoveries of transition metal complexes in which hydride, alkyl, olefin, allyl, etc., function as ligands makes the proposed surface intermediates appear quite ordinary. One could refer to the species at the right of eq 3 as a surface  $\sigma$ -alkyl but, for specificity, we shall call it "mono-adsorbed ethane." The species at the right of eq 2 will be called "1,2-diadsorbed ethane."

The combination of isotopic tracer studies, structural variation, and stereochemistry has been particularly useful in testing the *chemical* mechanism of heterogeneous catalytic reactions of hydrocarbons. The isotopic tracer studies have often given results of high directness and of high information content. Despite their low information content, the stereochemical results have been valuable because of the unusually high directness of stereochemical data. On the other

hand these studies have not as yet been very informative about the nature of the metal-carbon bonds in the intermediates of eq 2 and 3 or about the reason for differences among catalysts (but see Bond<sup>1</sup>).

The hydrogenation step itself involves *cis* addition of two hydrogen atoms. Formation of products of apparent *trans* addition results from side reactions.<sup>2,3</sup> At least in hydrogenations in the gas phase or in non-polar solvents, both hydrogen atoms add from the same side of the double bond and, moreover, both appear to add from the side of the original double bond which faces the catalyst.<sup>2,4</sup>

### The Use of Deuterium as an Isotopic Tracer

The question of the reversibility of reactions 1-4 immediately arises from consideration of the reaction between deuterium and ethylene. We assume rotation about the carbon-carbon bond in mono-adsorbed ethane to be fast. Suppose now that reaction -3 is much faster than 4. Alternation between mono- and diadsorbed ethane will have equilibrated all hydrogen atoms in desorbed ethane with the surface deuterium-hydrogen pool, D\*, H\*, to form a mixture of C<sub>2</sub>D<sub>6</sub> (called D<sub>6</sub>), C<sub>2</sub>HD<sub>5</sub> (D<sub>5</sub>), C<sub>2</sub>H<sub>2</sub>D<sub>4</sub> (D<sub>4</sub>), . . . C<sub>2</sub>H<sub>6</sub> (D<sub>0</sub>). The exact isotopic distribution depends upon the surface deuterium fraction (D\*)/[(D\*) + (H\*)]. If the rate of reaction -1 is zero, then, at complete hydrogenation, the fraction is one-third and the average formula C<sub>2</sub>H<sub>4</sub>D<sub>2</sub>. The isotopic distribution would be a smear in which D<sub>0</sub>, D<sub>1</sub>, . . . D<sub>6</sub> are all nonzero and D<sub>2</sub> is not at all near unity. If, on the other hand, reaction -1 is very fast, the surface fraction is unity and C<sub>2</sub>D<sub>6</sub> would be the only product. Clearly, exchange data are much easier to interpret (much higher directness) when the surface deuterium

(1) G. C. Bond, *Discussions Faraday Soc.*, **41**, 200 (1966).

(2) R. L. Burwell, Jr., *Chem. Rev.*, **57**, 895 (1957).

(3) G. V. Smith and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **84**, 925 (1962).

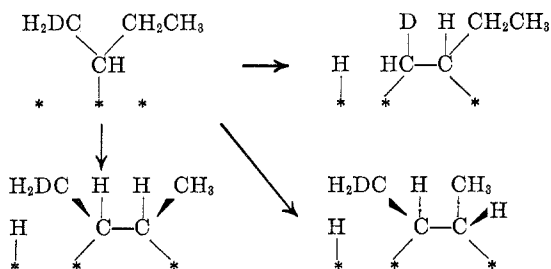
(4) G. V. Smith, *J. Catalysis*, **5**, 152 (1966).

fraction is unity than when it is lower.<sup>5</sup> Even a small amount of hydrogen can confuse the interpretation. Suppose all hydrogen atoms in cyclopentane to have been equilibrated with a surface pool:  $(D^*)/[(D^*) + (H^*)] = 0.97$ . Rather than a  $D_{10}$  of unity observed when the fraction is 1.00, one would observe  $D_{10}$  0.737,  $D_9$  0.228,  $D_8$  0.032,  $D_7$  0.002.

In practice, reaction -1 is largely inhibited during hydrogenation of olefins, and the surface deuterium fraction is well below unity. Further, for the pure gases, the reaction  $H_2 + D_2 = 2HD$  is fast on metallic catalysts at  $-78^\circ$  but it is strongly inhibited by olefins<sup>6</sup> and acetylenes.<sup>7</sup> One concludes that olefin is more strongly adsorbed than hydrogen from this and from the kinetics of olefin hydrogenation on many metallic catalysts (the rate is proportional to olefin concentration to a low or zero power and to hydrogen concentration to a higher power, often near unity).

Although reaction -4 is slow compared to 4 at temperatures below  $150^\circ$  or so, it can be studied by use of mixtures of alkanes and deuterium and appropriate conditions. If reaction -3 is even slower than reaction -4, then with ethane  $C_2H_5D$  is the initial product; if reaction -3 is much faster than -4, all hydrogen atoms in the ethane which desorb will have been equilibrated with  $D^*, H^*$  pool. During alkane exchange,  $(D^*)/[(D^*) + (H^*)]$  is very near unity and no information is lost by reaction of adsorbed alkane with  $H^*$  rather than with  $D^*$ . For this reason, isotopic exchange between  $D_2$  and alkanes has been rather extensively investigated both on evaporated metal films (mostly Kemball) and on conventional metal on alumina or on silica catalysts (mostly Burwell). The two types of materials give very similar results.

The study of more complicated alkanes and cycloalkanes leads to much more information than does ethane. One new feature can be introduced by discussion of the hydrogenation of 1-butene. This should adsorb as 1,2-diadsorbed butane, eq 2. Equation 3 can now form both 1-monoadsorbed and 2-monoadsorbed butane, and we are poorly informed as to the ratio. Reaction -3 of the latter species could either regenerate 1,2-diadsorbed butane or form *meso*- and *dl*-2,3-diadsorbed butane. Continua-



(5) E. F. Meyer and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **85**, 2881 (1963).

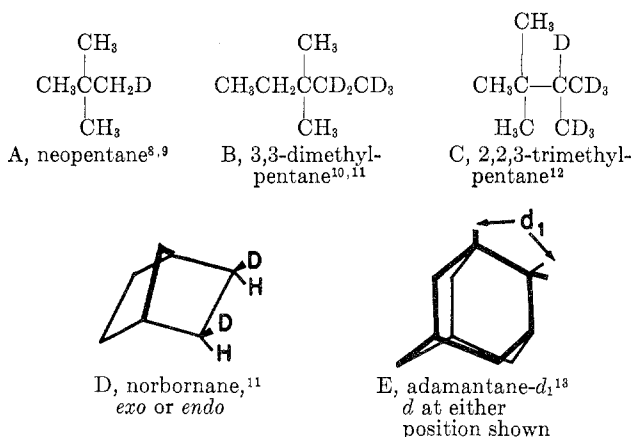
(6) For a review, see D. D. Eley, "Catalysis," Vol. III, P. H. Emmett, Ed., Reinhold Publishing Corp., New York, N. Y., 1955, pp 63 and 66.

(7) E. F. Meyer and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **85**, 2877 (1963).

tion of such processes could permit equilibration of all hydrogen atoms with the  $D^*, H^*$  pool. If reaction -2 is also fast, formation of exchanged 1-butene and of exchanged *cis*- and *trans*-2-butene would be observed.

### Isotopic Exchange between Alkanes and Deuterium

The *initial* products of the exchange at 0 to  $200^\circ$  of normal alkanes and of methylalkanes contain all exchanged species between alkane- $d_1$  and  $C_nD_{2n+2}$ ; however, those of certain other hydrocarbons contain no species more exchanged than A-E.



Monoadsorbed alkane readily reacts to form 1,2-diadsorbed alkane but only very slowly to form 1,3-diadsorbed alkane. Otherwise, A, B, and C would have given more extensively exchanged products. However, if one starts with cyclopropane, a molecule of much higher free energy, 1,3-diadsorbed alkane is a very probable intermediate in the hydrogenolysis to propane.<sup>14</sup> 1,4-Diadsorbed butane is a probable intermediate in the much slower hydrogenolysis of cyclobutane.<sup>9</sup> The major product of exchange of norbornane contains a pair of eclipsed deuterium atoms as shown in D. Thus, 1,2-diadsorbed alkanes readily form in eclipsed conformations. Staggered conformations are not favored. By its structure, adamantane E cannot form an eclipsed diadsorbed species and only adamantane- $d_1$  appears in the initial product of exchange.

### Isotopic Exchange between Cycloalkanes and Deuterium

What would one expect of cyclopentane? It should readily form the same eclipsed 1,2-diadsorbed cyclopentane as that formed directly by adsorption of cyclopentene (Figure 1). Let us divide the hydrogen atoms of cyclopentane into two sets, H and h, each consisting of all hydrogen atoms on one side of the ring. Con-

(8) C. Kemball, *Trans. Faraday Soc.*, **50**, 1344 (1954).

(9) H. C. Rowlinson, R. L. Burwell, Jr., and R. H. Tuxworth, *J. Phys. Chem.*, **59**, 225 (1955).

(10) J. A. Roth, B. Geller, and R. L. Burwell, Jr., *J. Res. Inst. Catalysis, Hokkaido Univ.*, **16**, 221 (1968).

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

(12) R. L. Burwell, Jr. and W. S. Briggs, *ibid.*, **74**, 5096 (1952).

(13) K. Schrage and R. L. Burwell, Jr., *ibid.*, **88**, 4555 (1966).

(14) J. Newham and R. L. Burwell, Jr., *J. Phys. Chem.*, **66**, 1438 (1962).

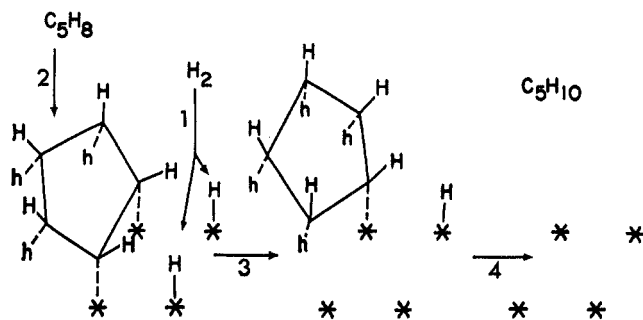


Figure 1. The hydrogenation of cyclopentene by the Horiuti-Polanyi mechanism.

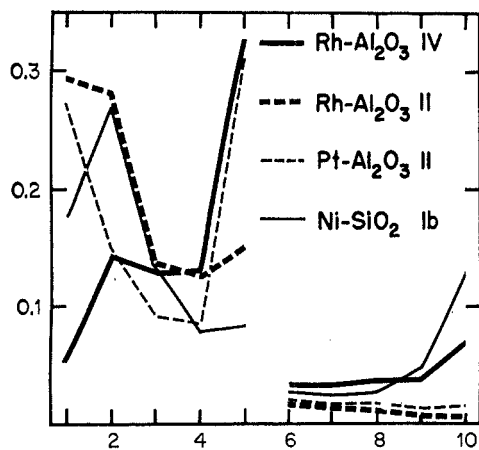


Figure 2. Isotopic exchange between deuterium and several supported metal catalysts: Rh IV at 86°, Rh II at 85°, Pt II at 78°, and Ni Ib at 70°.  $x$  axis, number of deuterium atoms exchanged;  $y$  axis, fraction of total exchange.

continued alternation between mono- and diadsorbed cyclopentane would lead to exchange of all hydrogen atoms of the set into which monoadsorbed cyclopentane was formed. No mechanism so far discussed in this paper can lead to initial products which contain molecules with exchange in both sets, *e.g.*,  $C_5D_3d_5$  or  $C_5H_2D_3h_1d_4$ . Such products could form in two or more periods of adsorption and, for this reason, most of our exchange runs are at conversions as low as permitted by analytical necessities. This has the additional advantage of keeping isotopic dilution of  $D_2(g)$  and  $D^*/H^*$  low.

Thus,  $D_5$  should be substantial and  $D_6$ – $D_{10}$ , zero. At lower temperatures, as first observed by Kemball,<sup>15</sup>  $D_5$  is generally substantial and  $D_6$  small, as shown for rhodium, platinum, and nickel in Figure 2.<sup>8</sup> With palladium, at lower temperatures,  $D_5$  is large,  $D_6$  and  $D_7$  are very small, and there is a small maximum at  $D_8$  and a large one at  $D_{10}$ . This is shown in Figure 3 for palladium on alumina.<sup>11,16</sup> A pattern close to those at 40° was reported for evaporated palladium film at 0°

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

(16) K. Schrage and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **88**, 4549 (1966).

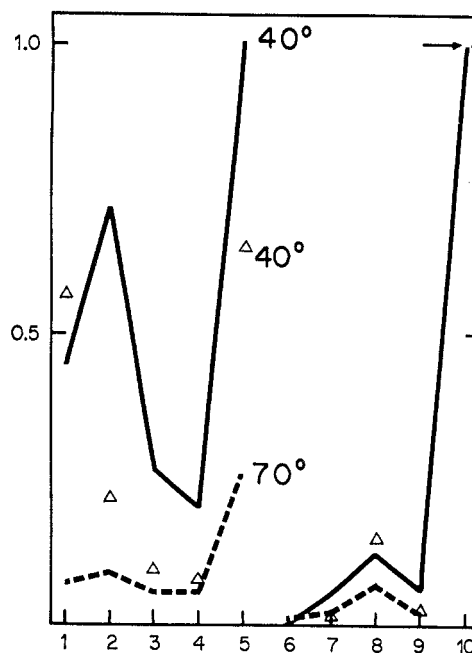


Figure 3. Effect of temperature on the isotopic distribution pattern resulting from the exchange of cyclopentane on a palladium on alumina catalyst (full and dashed lines). Triangles represent another palladium on alumina catalyst. The patterns are corrected for isotopic dilution and normalized to 1.0 at  $D_{10}$ .  $x$  axis, number of deuterium atoms exchanged;  $y$  axis, relative concentration.

by Anderson and Kemball.<sup>15</sup> With increasing temperature  $D_{10}$  becomes increasingly predominant, as may be seen by comparing the full and the dashed lines in Figure 3.

Figures 2 and 3 contain distribution patterns at the same operating conditions for two different preparations each of rhodium and palladium catalysts. They illustrate the observation that the isotopic distribution patterns vary not only with the metal but also with the support and with the conditions of preparation and pretreatment. With palladium there are clearly at least five separate processes involved<sup>16</sup>

	$n$ in $p_{D_2}^{-n}$	$E_a$ , kcal
(i and ii) two processes giving $d_1$ , $d_2$ , and $d_3$	0.4–0.5	10.5
(iii) a process giving $d_5$	0.85	14.8
(iv) a process giving $d_8$	1.2	20.4
(v) a process giving $d_{10}$	0.85	22.7

where the central column gives the kinetic dependence upon  $p_{D_2}$ .

The uncorrelated changes in the relative contributions of the five processes (partly evident in Figure 3) constitute particularly strong evidence for catalyst heterogeneity. That is, different sites must lead to each of the five processes. The differences may involve differences in crystallographic plane, in particle size, or in surface point defects. Differences in processes i, ii, and iii appear to result from differing values of  $r_{-3}/r_4$ , the value being the largest at the sites of iii.

The results with 3,3-dimethylpentane and cyclopentane correctly predict what should be observed with 1,1-dimethylcyclopentane on palladium: maxima at

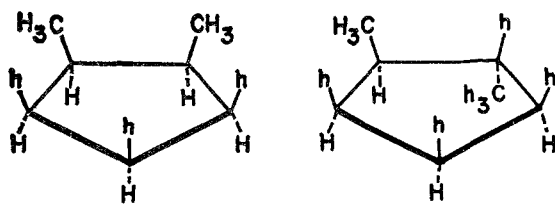
$D_4$  and  $D_8$  and a small maximum at  $D_6$ , *i.e.*, the gem-dimethyl groups do not exchange with the ring.<sup>11,16</sup>

If one assumes diadsorbed cyclohexane to involve some form of a boat conformation so as to permit formation of eclipsed diadsorbed cyclohexane, then cyclohexane has two sets of hydrogen atoms,  $C_6H_6h_6$ , one set on each side of the ring. All of one set could exchange in one period of residence on the surface, and process  $v$  should lead to  $d_{12}$ . In fact, on palladium at about  $40^\circ$ , maxima appear at  $D_6$  and  $D_{12}$ . The ratio  $D_{12}/D_6$  (unlike  $D_{10}/D_5$  in cyclopentane) is substantially affected by the pressure of deuterium.<sup>13</sup>  $D_{12}/D_{11}$  (unlike  $D_{10}/D_9$  in cyclopentane) is large only at the lowest values of  $p_{D_2}$ . This is what one would expect considering that the reaction, monoadsorbed  $\rightarrow$  diadsorbed, would be more difficult with cyclohexane because of the eclipsing strain introduced in converting chair-form monoadsorbed to boat-form diadsorbed.

We have assumed only *cis*-eclipsed diadsorbed cyclohexane to be possible since the *trans* form would be of high energy. However, with a large enough ring, both forms should appear readily. Such cycloalkanes would have but one set of hydrogen atoms because *trans*-eclipsed diadsorbed would transfer the carbon-surface bond from one side of the ring to the other. Cyclooctane possesses a sufficiently large ring in this sense. On palladium<sup>11</sup> all  $D_i$  are very small except  $D_1$ ,  $D_2$ , and  $D_{16}$ . The latter is heavily predominant at  $65$ – $170^\circ$ . Even with cycloheptane,  $D_{14}$  is heavily predominant,  $D_3$  to  $D_{13}$  are small, and the break between  $D_7$  and  $D_8$ , although visible, is small.

The exchange pattern of methylcyclopentane on palladium is informative. The representation of 1,7-diadsorbed methylcyclopentane in Figure 4 shows that methylcyclopentane has two sets of hydrogen atoms,  $C_6H_3h_4$ . Reactions  $-4$ , ( $-3$  and  $3$  repeated), and  $4$  would lead to a maximum exchange of four hydrogen atoms if initial adsorption is into the  $h$  set and of eight if into the  $H$  set. Figure 4 shows such maxima and, in addition, a maximum at  $C_6D_3d_4$  from process  $v$ .<sup>11,16</sup>

On these principles, *trans*-1,2-dimethylcyclopentane should have two sets of hydrogen atoms representable as  $C_7H_7h_7$  and *cis*-1,2-dimethylcyclopentane should have two sets,  $C_7H_{11}h_3$ . The expected maxima corre-



sponding to one-set exchange appear in the unepimerized but exchanged material:  $D_7$  for *trans*-1,2-dimethylcyclopentane as the reactant and  $D_3$  and  $D_{11}$  for *cis*.<sup>17</sup>

A number of polymethylcyclopentanes and cyclohexanes have been run and the maxima expected for

(17) R. L. Burwell, Jr., and K. Schrage, *Discussions Faraday Soc.*, **41**, 215 (1966).

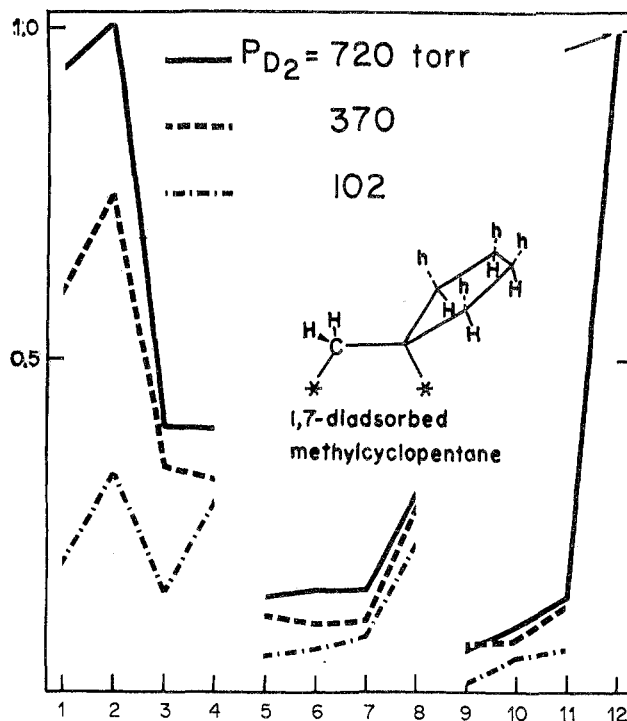
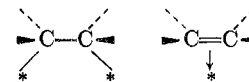


Figure 4. Isotopic distribution patterns for methylcyclopentane on palladium on alumina. The partial pressure of hydrocarbon was 30 Torr, that of deuterium, as shown; the temperature was  $40^\circ$ . The patterns are corrected for isotopic dilution and normalized to 1.0 at  $D_{12}$ .  $x$  axis, number of deuterium atoms exchanged;  $y$  axis, relative concentration.

one-set exchange have been seen except for a few which were obscured by large, adjacent maxima.<sup>10,11,13,18,19</sup>

There is an uncertainty in the elaborated Horvut-Polanyi mechanism. When the structure of olefin  $\pi$  complexes of transition metals was discovered, it was natural to suggest that what had been represented as eclipsed 1,2-diadsorbed alkane was, rather, a  $\pi$  complex to one surface atom.<sup>18-21</sup> However, the surfaces of metals present the possibility of polynuclear bonding not present in mononuclear complexes. The known structures of polynuclear complexes of acetylenes present a wide variety of binding but, in geometry, the complexes look more like disubstituted olefins than  $\pi$ -complexed acetylenes.<sup>22,23</sup>

The difference in geometry between the hydrocarbon portion of eclipsed diadsorbed alkane and that of  $\pi$ -complexed olefin (even if planar) is not large, and both



species lead to the same predictions for most hydro-

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

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

(20) D. K. Fukushima and T. F. Gallagher, *J. Am. Chem. Soc.*, **77**, 139 (1955).

(21) J. J. Rooney and G. Webb, *J. Catalysis*, **3**, 488 (1964).

(22) R. L. Burwell, Jr., and K. Schrage, *J. Am. Chem. Soc.*, **87**, 5253 (1965).

(23) Discussion by G. C. Bond, R. L. Burwell, Jr., P. Cossee, C. Kemball, J. J. Rooney, N. Sheppard, and P. B. Wells, *Discussions Faraday Soc.*, **41**, 249 (1966).

Table I  
Isotopic Exchange<sup>a</sup> (%) on Palladium on Alumina<sup>8</sup>

	Bicyclo[3.3.0]octane <sup>b</sup>	Bicyclo[3.3.1]nonane <sup>c</sup>
D <sub>0</sub>	93.44	97.77
D <sub>1</sub>	0.18	0.432
D <sub>2</sub>	0.36	0.051
D <sub>3</sub>	0.27	0.120
D <sub>4</sub>	0.12	0.080
D <sub>5</sub>	0.15	0.105
D <sub>6</sub>	0.30	0.088
D <sub>7</sub>	0.54	0.058
D <sub>8</sub>	1.45	0.384
D <sub>9</sub>	0.33	0.086
D <sub>10</sub>	0.42	0.447
D <sub>11</sub>	0.12	0.050
D <sub>12</sub>	0.30	0.334
D <sub>13</sub>	0.54	0.000
D <sub>14</sub>	1.45	0.000

<sup>a</sup> Uncorrected for isotopic dilution. <sup>b</sup> Temperature 68°,  $p_{HC}$  36 mm,  $p_{D_2}$  714 mm. <sup>c</sup> Temperature 50°,  $p_{HC}$  8 mm,  $p_{D_2}$  100 mm. Pressures are partial pressures of hydrocarbon and deuterium in a flow reactor.

carbons. However, there is a group of cycloalkanes the conversion of which to cycloalkenes needed in the  $\pi$ -complex model is abnormally endothermic (relative to cyclopentane  $\rightarrow$  cyclopentene) and yet which can form eclipsed diadsorbed species with no additional strain.<sup>24</sup>

Experiments with these hydrocarbons should provide a test of the 1,2-diadsorbed and the  $\pi$ -complex models provided that the strain energy in the olefins is not completely compensated by strength of binding in the  $\pi$  complex. This seems unlikely. Further, one would need assume that the strain energy is fully compensated in the highly strained *trans*-cycloheptene since the  $\pi$  complex of this must be assumed to form readily if D<sub>7</sub> and D<sub>8</sub> are to be very small *vs.* D<sub>14</sub> in exchanged cycloheptane. On the other hand, one must assume that it is not compensated in adamantene since adamantene exhibits single-atom exchange only.

In bicyclo[3.3.1]nonane,<sup>10,13,17,22</sup> the eight-atom H set (Table I) could exchange *via* relatively unstrained, eclipsed diadsorbed bicyclononanes. In the  $\pi$ -complex model, one needs the bridgehead, anti-Bredt bicyclononene which has a strain energy of 12 kcal.<sup>25</sup> As shown in Table I, a maximum at D<sub>8</sub> is prominent on palladium. The maximum also appears on nickel, platinum, and rhodium although, as with other cyclic hydrocarbons, the value at complete one-set exchange is smaller and those of D<sub>1</sub>, D<sub>2</sub>, and D<sub>3</sub> larger than on palladium.

(24) Cyclooctane  $\rightarrow$  *trans*-cyclooctene and norbornane  $\rightarrow$  norbornene are examples. For relevant heats of hydrogenation see R. B. Turner and W. R. Meador, *J. Am. Chem. Soc.*, **79**, 4116, 4133 (1957).  
(25) P. M. Lesko and R. B. Turner, *ibid.*, **90**, 4315 (1968).

We conclude that diadsorbed alkane does not have the structure of a *planar*  $\pi$  complex although we cannot exclude a structure substantially distorted toward that of eclipsed diadsorbed alkane. Some intermediate type of structure might well be stabilized by the maze of orbitals available at the surface of a metal, and a structure of this type would explain why eclipsed rather than staggered is favored. Any further resolution of this problem seems difficult with present techniques.<sup>10,23</sup>

### Racemization and Epimerization

On nickel<sup>9,12,26</sup> and palladium,<sup>11</sup> almost every molecule of (+)-3-methylhexane which exchanges at the tertiary position is racemized. On nickel,<sup>22</sup> the kinetic orders of racemization and exchange are both of the following form, where  $\alpha$  is the optical rotation and  $L$  is the flow rate.

$$\ln(1/D_0) \simeq \ln(\alpha_0/\alpha) = (k/L)p_{H_2}^{-0.6}p_{HC}^{0.33}$$

Since there is some stereochemical resemblance between this racemization and two-set exchange in cyclopentane, it seemed useful to try to find one mechanism which could account for both processes.<sup>11,26</sup> The possibility of one mechanism is strengthened by the observation that epimerization accompanies exchange of polymethylcyclopentanes.<sup>13,18</sup> This was examined in detail for *cis*- and *trans*-1,2-dimethylcyclopentane on palladium on alumina.<sup>17</sup> At low conversions, the products consist of (a) unepimerized di-

(26) R. L. Burwell, Jr., and R. H. Tuxworth, *J. Phys. Chem.*, **60**, 1043 (1956).

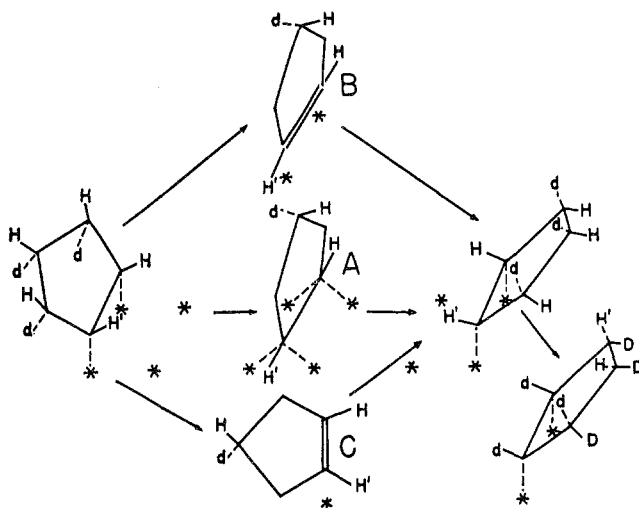
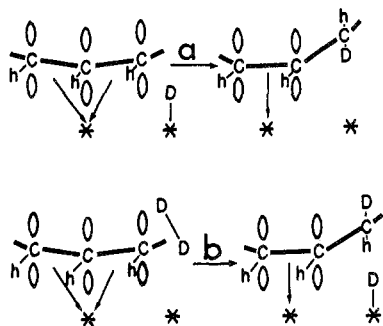


Figure 5. Roll-over mechanism (eq 5).

Figure 6.  $\pi$ -Allyl mechanism.

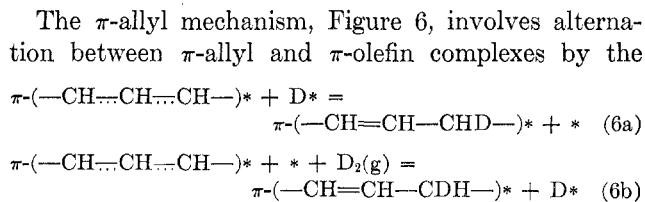
methylcyclopentane exhibiting one-set exchange; (b) *cis*- and *trans*-dimethylcyclopentanes which are almost completely  $C_7D_{14}$  and which appear in the ratio 1:3.

### Mechanism of Two-Set Exchange, Racemization, and Epimerization

Several early mechanisms for these processes proved incompatible with later data and, at present, two mechanisms, roll-over<sup>10,13,17</sup> (Figure 5) and  $\pi$  allyl<sup>18,19</sup> (Figure 6), accommodate the results; neither has been rigorously eliminated. Most of the tests of these mechanisms come from data on palladium because it gives much more two-set exchange and sharper maxima in  $D_4$ .

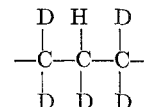
Desorption of olefin by reaction -2 and its readsorption on the other side of the ring, reaction 2, is a form of the roll-over mechanism. For example, cyclopentene- $d_3$ ,  $C_5H_5d_3$ , could desorb, readsorb on the other side, and lead to  $C_5H_5D_3$ . Ignoring the heat of adsorption of hydrogen, the minimum activation energy for this process would be 27 kcal/mol, the heat of hydrogenation of cyclopentene, whereas the observed activation energy on palladium is 20 kcal/mol (see process iii of the section Isotopic Exchange between Cycloalkanes and Deuterium). "Olefin" oriented with the plane of the olefin perpendicular to the surface and bound with a rather small binding energy would provide an intermediate or transition state which could transfer

adsorption from one side of the plane of the ring to the other. Since the needed binding energy is small, it seems almost inevitable that one or more such species contributes to two-set exchange. Figure 5 shows three conceivable species. A has coordination somewhat like that of the dimer of aluminum trimethyl. B and C are edge- and end-bonded olefin in which we imagine some interaction between empty surface orbitals and the filled  $\pi$  orbital of the olefin.

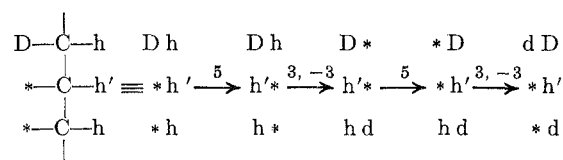


simultaneous progress of two different elementary reactions of different steric consequences: in eq 6a a deuterium atom adds to  $\pi$  allyl from below and in eq 6b a molecule of deuterium reacts with  $\pi$  allyl and a vacant site to add a deuterium atom from above. One might have some reservations about the possibility of a sufficiently low  $E_a$  for (6b). There may be steric difficulties and the D-D bond must be stretched considerably before much bonding can occur.

What would be the consequences of the  $\pi$ -allyl mechanism in the exchange of an isolated trimethylene unit of a ring? Repetition of (6a) and (6b) leads to



and the hydrogen atom above the plane on the central carbon atom can never be exchanged. But the roll-over mechanism gives the same result, as may be seen from



The symbolism is evident from the first two columns at the left which are an identity. The numbers refer to the steps in the Horiuti-Polanyi mechanism and 5 to the roll-over reaction.

Rooney<sup>19</sup> has investigated the interesting compound 1,1,3,3-tetramethylcyclohexane which has an isolated trimethylene unit. At lower temperatures, a break follows one-set exchange ( $d_3$ ),  $D_5$  is large, and  $D_6$  is nearly negligible, in accord both with the  $\pi$ -allyl and the roll-over mechanisms.

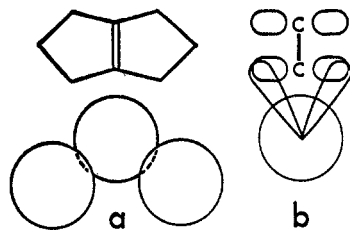
If the h atom at the right of the  $\pi$ -allylic species of Figure 6 is replaced by methyl, process 6b leads to inversion of configuration of the carbon atom at the right. Thus, epimerization of dimethylcyclopentanes and racemization of (+)-3-methylhexane will follow. Roll-over gives the same result as may be seen in replacing one of the H' atoms at the left of Figure 5 by methyl.

A key point is that roll-over transfers two atoms from the H set into the h set, as shown in Figure 5. Thus, a single roll-over of diadsorbed cyclopentane gives  $C_5H_2D_3$  as the most exchanged species. We suggest that  $C_5H_2D_3$  is formed on palladium by this process at sites of low probability of roll-over. At other sites of higher probability, successive roll-overs combined with alternation of the position of adsorption by reactions 3 and  $-3$  will lead to  $C_5D_{10}$ . It is difficult to see how the  $\pi$ -allyl mechanism can generate a maximum at  $D_3$ , but it can readily generate one at  $D_{10}$  by processes 6a and 6b so taken as to result in migration of the position of adsorption. As will be seen,  $\pi$ -allyl and multiple roll-over can both lead to complete exchange of units with four or more methylenes in a ring (e.g., 1,1-dimethylcyclopentane); only trimethylene is restricted.

Bicyclo[3.3.1]nonane contains isolated trimethylene units and it exhibits maxima at  $D_{10}$  and  $D_{12}$ . The latter involves exchange of the g and the h sets as well as the H set but not atoms h' and g' (Table I).  $D_{10}$  probably involves exchange of the g or the h sets. Again, both  $\pi$ -allyl and roll-over accord with the results.

*cis*-Bicyclo[3.3.0]octane is of interest because epimerization at just one carbon atom would generate *trans*-bicyclo[3.3.0]octane, a molecule too strained to be significant here. Roll-over of 1,2-diadsorbed *cis*-bicyclooctane is excluded for this reason; it gives diadsorbed *trans*-bicyclooctane. Roll-over of 1,5-diadsorbed *cis*-bicyclo[3.3.0]octane by species A and B of Figure 5 is impossible sterically.

Bicyclo[3.3.0]octane exchanged on palladium shows about equal values for  $D_3$  and  $D_{14}$  (Table I). Roll-over *via* C shown below side on (a) and edge on (b) accords



with these results.  $\pi$  Allyl probably accords, although one might have expected strain in  $\pi$ -complexed bicyclo[3.3.0]oct-1-ene to restrict exchange to one ring. An investigation of 1-methylbicyclo[3.3.0]octane would be of interest since it could not give multiset exchange by C. Nickel, platinum, and rhodium give little exchange beyond  $d_6$ ,  $D_3$  is smaller than with palladium, and  $D_1$  and  $D_2$  are much larger. Palladium seems uniquely resistant to the effects of various types of steric hindrance which might impede conversion of monoadsorbed into diadsorbed.

### Steric Aspects of Sites

Many suggested intermediates or transition states cannot readily form upon a densely packed plane such as the (111) plane of face-centered cubic metals.<sup>23</sup> A  $\pi$ -complexed *trans*-2-butene, 1,2,3- $\pi$ -allylcyclopentane, or any of the roll-over forms of Figure 5 will of necessity

put hydrogen atoms which are bonded to carbon and not to metal closer to the surface than the carbon atoms which are presumed to be bonded to metal. We know that the effects of surface-substrate interaction are real as in the preferential formation of *cis*-*vs.* *trans*-2-butene in the hydrogenation of methylallene.<sup>5</sup> However, as just one example of a number,<sup>23</sup> *trans*-di-*t*-butylethylene is readily hydrogenated even though the double bond can hardly approach a densely packed plane at all closely.<sup>27</sup> Reactions of this type may involve atoms of the surface at edges or the like.<sup>23</sup> Such a process is shown above for roll-over of bicyclooctane by C.

### Reaction of Deuterium with Olefins

Of the many examples under this heading, we will consider just two cases that are closely related to the concepts so far discussed. As mentioned earlier, reactions 3 and  $-3$  generate  $H^*$  which exchanges only slowly with gas-phase  $D_2$  because desorption of HD is inhibited by olefin. Therefore,  $D^*/H^*$  is relatively small and interpretation of isotopic exchange patterns may be difficult.

For example, in the batch reaction between undiluted liquid cyclopentene and deuterium gas in an agitated reactor with platinum on alumina as the catalyst,<sup>28</sup> a sample at 15% hydrogenation also contained about 15% exchanged cyclopentene, mostly  $d_1$ . Formation of cyclopentene-*d* lowered  $D^*/H^*$  beyond that resulting from reactions 3 and  $-3$ . Correspondingly,  $D_{av}$  in the cyclopentane was only 1.2,  $D_1 + D_2$  was 0.68, and  $D_5$  was so small that one could not identify a break following it. When, however, a mixture of cyclopentene, tetrahydrofuran, and  $D_2O$  in proportions by volume of 0.1, 1.5, and 0.1 was treated with deuterium to 15% hydrogenation,  $D_{av}$  was 2.55. Clearly,  $D_2O$  had exchanged with  $H^*$  and, as shown by analysis of the distribution pattern,  $D^*/H^*$  had increased to about 0.83/0.17.  $D_5$  was now large enough to show the expected sharp break following it.  $D^*/H^*$  was large enough so that, with some confidence, one could convert the  $D_i$ 's into the fractions actually equilibrated with the  $D^*,H^*$  pool.

When  $CH_3COOD$  was used as the solvent, the cyclopentane was even more extensively exchanged:  $D_0$  0.075,  $D_1$  0.159,  $D_2$  0.269,  $D_3$  0.154,  $D_4$  0.150,  $D_5$  0.138,  $D_6$  0.021. One cannot interpret such a pattern with a single value of  $D^*/H^*$ . If  $D^*/H^*$  be much below 0.9/0.1, one cannot have  $D_5$  almost as large as  $D_4$ . But a value anywhere nearly as large as 0.9/0.1 cannot give  $D_0$  and  $D_1$  large enough relative to  $D_2$ . Clearly, one set of sites gives mainly addition of two D(H) atoms, formation of cyclopentene-*d*, and relatively slow exchange between  $H^*$  and DOAc. There is another set of sites upon which  $r_{-3}/r_4$  is much larger and ex-

(27) W. H. Puterbaugh and M. S. Newman, *J. Am. Chem. Soc.*, **81**, 1611 (1959).

(28) J. J. Phillipson and R. L. Burwell, Jr., *Preprints, Div. Petroleum Chem., Am. Chem. Soc.*, **11**, A-39 (1966).

change with DOAc is relatively much faster. Thus,  $D^*/H^*$  is smaller on the first set of sites. Since platinum catalysts rarely (but see the next paragraph) lead to much formation of isomeric olefins,<sup>29</sup> exchanged olefin is not formed here by the simple extension of the Horiuti-Polanyi mechanism given earlier.

In the platinum-catalyzed reaction between deuterium and  $\Delta^{1(9)}$ -octalin and  $\Delta^9$ -octalin, the extent of exchange of original hydrogen atoms of the octalins was low enough to make  $D^*/H^*$  high enough to permit calculation of the true equilibration fractions.<sup>3</sup> Hydrogenation of  $\Delta^9$ -octalin is very slow. A small amount of product is *cis*-decalin-9,10- $d_2$ , but most appears to be *cis*- and *trans*-decalin formed by hydrogenation of a preliminary isomerization product,  $\Delta^{1(9)}$ -octalin. In

(29) A. S. Hussey, T. A. Schenach, and R. H. Baker, *J. Org. Chem.*, **33**, 3258 (1968).

support of this, most of the *cis*- and all of the *trans*-decalin have at least three hydrogen atoms which have equilibrated with  $D^*, H^*$ .

In reactions between deuterium and dialkylacetylenes, butadiene, and methylallene on palladium,  $D^*/H^*$  is large. Rapid progress of  $H^* + D^* = HD + 2^*$  is not responsible for this; in fact, desorption of HD is heavily inhibited. Consequently, results are relatively simply interpreted and the mechanisms of these hydrogenations are known in some detail.<sup>5,7</sup> Just one aspect will be mentioned. If 2-butyne is hydrogenated with a mixture of  $H_2 + D_2$ , very little HD appears in the gas phase and one might be tempted to suppose that  $H_2$  and  $D_2$  add molecularly to the butyne. However, the product is a mixture of *cis*-2-butene- $d_0, -d_1$ , and  $-d_2$  in random proportions. Thus,  $H_2$  and  $D_2$  are dissociated into atoms before they add.

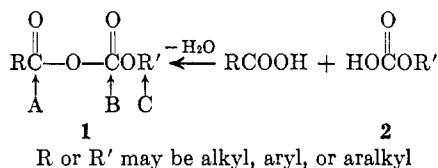
## The Carboxylic Carbonic Anhydrides and Related Compounds

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The carboxylic carbonic anhydrides **1** may be formally regarded as derived from a carboxylic acid, RCOOH, and a monoester of carbonic acid, **2**. A few isolated examples of these anhydrides have been known for a



long time, but thorough investigations of their preparation, isolation, synthetic properties, and mechanistic behavior have been reported only in recent years.

The anhydrides **1** are compounds of considerable theoretical and practical interest. They can be attacked by nucleophiles at the carboxyl carbonyl (A) or the carbonate carbonyl (B); their first synthetic usefulness was in the formation of peptide linkages, by the attack of the amino group of a protected amino acid at A.<sup>1</sup> The nucleophile can be a carbanion,<sup>2</sup> and the mixed anhydride **1** is particularly useful in cases where the acyl group contains structures that would be sensitive to reagents normally used to convert carboxylic acids to acid chlorides;<sup>3</sup> **1** may be prepared at low temperatures under practically neutral conditions.

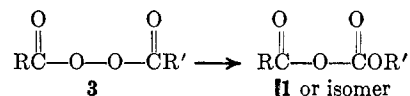
(1) The extensive applications of **1** in peptide synthesis are summarized by N. F. Albertson, *Org. Reactions*, **12**, 172 (1962), and by M. Bodansky and M. A. Ondetti, "Peptide Synthesis," Interscience Publishers, New York, N. Y., 1966, p 88 ff.

(2) D. S. Tarbell and J. A. Price, *J. Org. Chem.*, **21**, 144 (1956); **22**, 245 (1957); *Org. Syn.*, **37**, 20 (1957).

(3) Cf. J. H. Boothe, *et al.*, *J. Am. Chem. Soc.*, **81**, 1006 (1959).

The anhydrides have also been used to acylate inorganic azides,  $H_2S$ , thiols, hydroxyl groups, and phosphates.

It is now known<sup>4</sup> that one of the important modes of decomposition of diacyl peroxides **3** is by the so-called carboxyl inversion reaction, to form the carboxylic carbonic anhydrides **1**, which may be isolated as such or converted to other products, depending on conditions. Denney<sup>4a</sup> has described conditions under which an acid, R'COOH, can be readily converted to the next



lower alcohol, R'OH, by the above process, followed by hydrolysis of the anhydride **1**.

From the mechanistic side, a study of the modes of decomposition of **1** as a function of structure, nucleophiles present, and solvent and Lewis acids has given much useful information about carbonyl reactivity, nucleophilic reactivity, and the behavior of ion pairs. By suitable substitution the cleavage of **1** can be made to occur at C (in **1**), *i.e.*, with alkyl-oxygen cleavage, depending on the solvent and presence of catalysts. The study of analogs of **1**, such as **4**, **5** and **6**, has given further synthetically and mechanistically useful information.

(4) For leading references, see (a) D. B. Denney and N. Sherman, *J. Org. Chem.*, **30**, 3760 (1965); (b) F. D. Greene, *et al.*, *J. Am. Chem. Soc.*, **86**, 2080 (1964); (c) P. D. Bartlett and F. D. Greene, *ibid.*, **76**, 1088 (1954); (d) J. E. Leffler, *ibid.*, **72**, 67 (1950); (e) C. Walling, *et al.*, *ibid.*, **87**, 518 (1965).