



Title	ISOTOPIC EXCHANGE BETWEEN DEUTERIUM AND SOME CYCLIC HYDROCARBONS ON METALLIC CATALYSTS
Author(s)	ROTH, Jerome A.; GELLER, Baltes; BURWELL, JR. Robert L.
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 16(1), 221-243
Issue Date	1968
Doc URL	<a href="http://hdl.handle.net/2115/24858">http://hdl.handle.net/2115/24858</a>
Type	bulletin (article)
File Information	16(1)_P221-243.pdf



[Instructions for use](#)

## ISOTOPIC EXCHANGE BETWEEN DEUTERIUM AND SOME CYCLIC HYDROCARBONS ON METALLIC CATALYSTS

By

Jerome A. ROTH, Baltes GELLER,  
and Robert L. BURWELL, JR.

Department of Chemistry, Northwestern University,  
Evanston, Illinois, 60201, U. S. A.

(Received December 20, 1967)

### Abstract

Isotopic exchange between deuterium and the following hydrocarbons, cyclopentane, bicyclo [3.3.0] octane, bicyclo [3.2.1]octane, bicyclo [3.3.1] nonane and cyclopentylcyclopentane has been investigated on supported rhodium, palladium, platinum and nickel catalysts at about 75°C.

The primary processes in isotopic exchange are dissociative adsorptions of deuterium and alkane. The next most important process is the dissociative surface reaction which converts monoadsorbed alkane to diadsorbed alkane. The geometry of diadsorbed alkane is intermediate to an undetermined degree between that of eclipsed alkane and of  $\pi$ -complexed olefin but not very close to the latter. The surfaces of the metals each possesses two or more types of sites with different ratios of the rates of reaction of monoadsorbed alkane to diadsorbed alkane and to gas phase alkane. The ratios seem to vary from metal to metal and to depend upon any strain involved in forming diadsorbed alkane. Palladium is less strain-sensitive than the other metals of the present group.

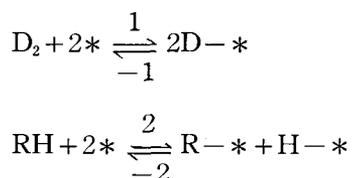
Most of the exchange on rhodium, platinum and nickel accords with the predictions of the reactions mentioned above. More highly exchanged hydrocarbons also appear in the initial products, particularly on palladium. The formation of these more exchanged products is discussed with reference to their possible formation by roll-over and by  $\pi$ -allyl mechanisms.

During the past fifteen years or so, studies of isotopic exchange between deuterium and a wide variety of saturated hydrocarbons on metallic catalysts have contributed substantially to our understanding of reactions between hydrocarbons and hydrogen on such catalysts.<sup>1)</sup> Since isotopic exchange between deuterium and alkanes is presumed to involve partial reversal of olefin hydrogenation, these studies have contributed, in particular, to an understanding

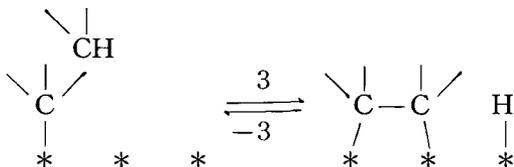
J. A. ROTH, B. GELLER and R. L. BURWELL, JR.

of the mechanism of the hydrogenation of olefins.<sup>2)</sup>

A reasonably good consensus has developed with respect to the broader aspects of mechanism in these reactions. Basically, this represents an extension of the original Horiuti-Polanyi proposals. For the most part, the areas of controversy have shrunk to more minor aspects of mechanism. Thus, there is general agreement that the initial processes in isotopic exchange involve dissociative adsorption of deuterium and alkane



Simultaneous progress of reactions (1) and (2) would lead to formation of RD+HD. Under most conditions, it is clear that reaction (-1) is so much faster than (-2) that the surface ratio D-\* / H-\* remains very large as long as isotopic dilution of gas phase deuterium is small. In isotopic exchange of neopentane and adamantane,<sup>3)</sup> reactions (1) and (2) account for almost all of the products. With other alkanes, additional reactions are involved, the major of which is



Two different structures have been proposed for the diadsorbed alkane at the right, a) eclipsed diadsorbed alkane,<sup>4)</sup> b)  $\pi$ -complexed olefin.<sup>5,6)</sup> The differences in geometry between the two suggested structures are not large. We have argued that a strictly planar form of b) is not likely on palladium<sup>3)</sup> but some form intermediate between a) and b) may well be the correct one.<sup>2)</sup> The relative contributions of a) and b) may vary with the hydrocarbon, with the metal, and with the local site.

At the beginning of modern studies on isotopic exchange between deuterium and alkanes (1951), complexes between hydrocarbons or hydrocarbon radicals and transition metals were essentially unknown. Indeed, structures for such compounds were first proposed by catalytic chemists. In recent years large numbers of molecular complexes have been prepared. The variety of structures is now so great, that it is difficult to eliminate possible surface

*Isotopic Exchange between Deuterium and Cyclic Hydrocarbons*

structures by reference to molecular analogies.

The application of reactions (1), (2), and (3) to cyclopentane suggests that no more than five deuterium atoms should be exchanged in one period of adsorption of a molecule on the surface. Alternation between reactions (3) and ( $-3$ ) would exchange all of the hydrogen atoms on that side of the ring which is initially adsorbed but no intermediate mentioned above leads from one side of the ring to the other. There is indeed, in most cases, a maximum in the isotopic distribution at cyclopentane- $d_5$  but there are also species of higher degree of exchange among the initial products.<sup>1)</sup> Whatever process causes this seems to be related to that which causes racemization of optically active hydrocarbons and epimerization of such molecules as dimethylcyclopentanes.<sup>3,4)</sup>

Of the identified major processes in alkane exchange, this is the only one in which the proposed mechanisms are widely divergent. At present, the two mechanisms which accommodate the largest number of data are a  $\pi$ -allyl mechanism<sup>7)</sup> which we designate reaction (4) and a roll-over mechanism,<sup>3,8)</sup> reaction (5). In the  $\pi$ -allyl mechanism, the far side of the cyclopentane ring is exchanged by a *non-turn-over* process. That is, exchange of the far side hydrogen atoms is effected by the simultaneous progress of two separate reactions which interconvert the diadsorbed species and the  $\pi$ -allyl one. In one, a near-side hydrogen atom is added or removed, in the other, a far-side hydrogen atom. This is shown in Figure 1. The roll-over mechanism is a *turn-over process* as shown in Figure 2.

It seems clear then that many current mechanistic problems in the area of alkane exchange are related to somewhat subtle aspects of mechanism.

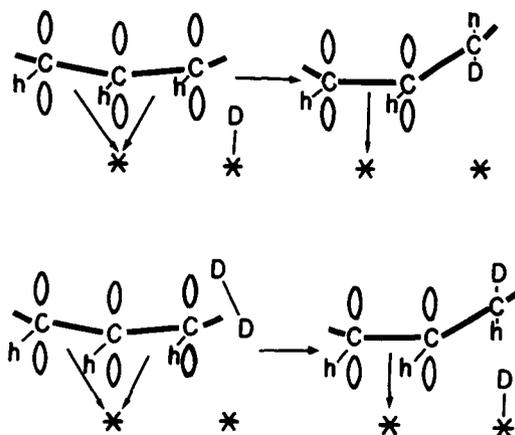


Fig. 1. The  $\pi$ -allyl mechanism.

J. A. ROTH, B. GELLER and R. L. BURWELL, JR.

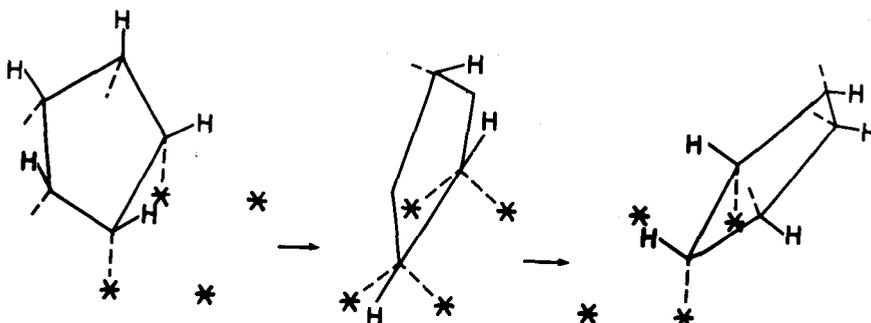


Fig. 2. The roll-over mechanism as exemplified by cyclopentane.

Further elucidation of these aspects should result from the study of molecules with special stereochemical relations among the various sets of hydrogen atoms. For this reason we have investigated the exchange of cyclopentane, cyclopentylcyclopentane, bicyclo[2.2.1]heptane, bicyclo[3.2.1]octane, bicyclo[3.3.0]octane and bicyclo[3.3.1]nonane on palladium, platinum, rhodium and nickel catalysts. We have worked as far as possible in the temperature range of about 75°C and we have not examined the effect of variation of temperature or partial pressures of the reactants. It would be very desirable to have kinetics studies in these systems but we have not yet done them.

### Experimental Section

The preparation of bicyclo[3.3.1]nonane has been described.<sup>3)</sup> *Cis*-bicyclo[3.3.0]octane was prepared by isomerizing cyclo-octa-1,5-diene to bicyclo[3.3.0]octene by lithium phenyl<sup>9)</sup> and hydrogenating the latter over palladium-charcoal in hexane. The product was purified by preparative gas chromatography on a Dow 20 silicone oil column at 110°C. The material was 98% pure by analytical chromatography. Bicyclo[3.2.1]octane was prepared by hydrogenating 2-hydroxymethylbicyclo[2.2.1]heptene (Aldrich Chemical Company) over nickel-alumina at 120°C and 100 atm. in a rocking autoclave and subjecting the product to a Wagner-Meerwein rearrangement with orthophosphoric acid at 160°. <sup>10)</sup> The resulting bicyclo-octene was hydrogenated and then treated with potassium permanganate in acetone to remove traces of olefin. Distillation followed by preparative gas chromatography gave a 90% yield of bicyclo[3.2.1]octane, 99.2% pure, m.p. 136°C.

Cyclopentylcyclopentane (Chemical Samples Company), purified by preparative gas chromatography was 99.8% pure. Cyclopentane (Phillips Research Grade), after washing with concentrated sulfuric acid and purification by pre-

*Isotopic Exchange between Deuterium and Cyclic Hydrocarbons*

parative gas chromatography was 99.95% pure. 3, 3-Dimethylpentane (Chemical Samples Company) was 99.99% pure and was used as received.

**Catalysts.** Two commercial catalysts were used, a nickel-silica catalyst (Harshaw Chemical Company) and a Baker rhodium-alumina, 0.5% rhodium. Rh-VI was a film of rhodium covering the inside of a glass tubing of 5 mm. inside diameter. It was prepared by the thermal decomposition of  $(\text{Rh}(\text{CO})_2\text{Cl})_2$  vapor on the glass held at 220°C. We are indebted to Prof. F. Basolo for the rhodium carbonyl chloride.

The other catalysts were prepared in standard fashion by impregnating a support with a solution of a compound of the transition metal and drying. Before use, the catalyst was reduced with hydrogen at the temperature shown in Table I. To avoid the use of inconveniently small amounts of catalyst,

TABLE I. Catalysts

No.	Support	Diluent	Metal <sup>a</sup> %	Final <sup>b</sup> %	Reduction Temp.	Mesh	Weight g
Rh-I	Alumina <sup>c)</sup>	Glass beads <sup>d)</sup>	0.5	0.45	250°	100-140	0.55
Rh-II	Silica <sup>e)</sup>	Silica	0.016	0.0032	480°	80-100	1.00
Rh-III	Silica <sup>e)</sup>	none	0.0016	0.0016	480°	80-100	1.00
Rh-IV	Filtros <sup>f)</sup>	none	0.016	0.016	450°	40-60	2.00
Rh-V	Filtros <sup>f)</sup>	Filtros	0.039	0.039	480°	40-60	2.00
Pt-I	Alumina <sup>g, h)</sup>	none	0.42	0.42	480°	80-100	1.00
Pt-II	Alumina <sup>g, i)</sup>	none	0.12	0.12	480°	80-100	1.00
Pt-III	Silica <sup>j)</sup>	none	0.24	0.24	480°	80-100	1.00
Pd-I	Alumina <sup>k)</sup>	Alumina	5.0	0.0025	350°	60-80	1.00
Pd-III	Alumina <sup>k)</sup>	Glass beads <sup>d)</sup>	5.0	m)	350°	60-80	m)
Ni-I	Silica	Filtros	42	5.1	490°	60-80	1.00

a) Wt. % of metal on the catalyst as prepared. b) Wt. % of metal after dilution.

c) "Baker" commercial preparation. The original catalyst pellets were non-uniform, most of the metal being concentrated near the outside of the pellet. d) Glass beads

of near the mesh size of the catalyst were heated in  $\text{HNO}_3\text{-H}_2\text{SO}_4$ , washed and ignited in air at 550° overnight. e) Davison Grade 70, wide-pore silica gel. Impregna-

tion with an amount of  $\text{RhCl}_3$  solution to give the desired rhodium content. f) Fil-

tros FS-140-L silica, Filtros Corporation, Rochester, N. Y., impregnation as in e).

g)  $\gamma$ -Alumina from Prof. A. S. Hussey, see *J. Org. Chem.*, **33**, 610 (1968). h) Impreg-

gnated with a solution of  $\text{K}_2\text{PtCl}_4$ . i) Impregnated with diaminodinitroplatinum (IV).

j) Wide pore silica impregnated with diaminodinitroplatinum (IV) in two portions with intervening activation. k) Harshaw Hard Alumina, Lot AL-0104 MT, impregnated

with a solution of palladium chloride. m) This catalyst had been prepared by K. Schrage, Catalyst IV, ref. 4. Various weights were diluted with glass beads several fold.

J. A. ROTH, B. GELLER and R. L. BURWELL, JR.

the catalyst was often diluted with inert support. The weight shown in the table is that of catalyst plus inert support. The wide pore silica gel used as a support, Davison Grade 70, is reported to have an average pore diameter of 140 Å. Filtros is a macroporous, low area siliceous support. Its average pore diameter is reported to be 65 microns.

Catalysts which differed in minor ways from those of Table I have a capital letter added to the catalyst designation. Rh-IA differed from Rh-I in being reduced at 380° and being 140–200 mesh. Rh-IIA was diluted to a final % 0.0016 and Rh-VA, to 0.0020. Ni-IB was reduced at 300° rather than 490°. Rh-IIA' was a new preparation according to the recipe for Rh-IIA.

**Apparatus.** The experimental procedure was similar to one previously used<sup>11</sup> except that hydrogen was purified by passage through palladium-silver alloy (25% silver). The gas then passed through a U-tube packed with Filtros, the pores of which were filled with the hydrocarbon to be evaporated. Since the U-tube was thermostatted, the exit hydrogen contained a fixed partial pressure of hydrocarbon. The total pressure was 750 Torr. After passage over the catalyst, the hydrocarbon was recovered for mass spectrographic analysis by condensing it in a cold trap. The gases were exposed neither to mercury vapor nor to greased stopcocks.

**Analysis.** Isotopic distribution patterns were determined at reduced ionizing voltages with a Consolidated 21–130 mass spectrometer.<sup>4,12</sup>

**Results with cyclopentane.** Table II presents data obtained with rhodium catalysts. In general, catalytic activity declined from run to run after initial activation of the catalyst. For example, run 101 was the second run on freshly reduced catalyst Rh-I; run 104, the fifth. The activity declined by a factor of about 4 between the two runs. The catalyst was retreated with hydrogen to 230° before run 107 but the catalytic activity was not increased. However, the pattern from run 107 closely resembled that from run 105. The decline with Rh-IA was smaller. This catalyst was first used in run 153. It was retreated with hydrogen at 300° before run 159. The isotopic distribution patterns of runs 154 and 155 resembled that of run 159. Run 179, with cyclopentane was the first run with catalyst Rh-IIA'. Before run 181 it was treated with hydrogen for 1 hour at 500°. Activities and exchange patterns were similar in the two runs. Other runs in the Table were on freshly reduced catalysts.

The sequence, runs 104 and 105, suggests that the relative yield of cyclopentane with six or more deuterium atoms increases with temperature. Other runs, not given in Table II, support this for other rhodium catalysts. We have not, however, examined this point systematically.

TABLE II. Isotopic Exchange Between Cyclopentane and Deuterium on Rhodium Catalysts

Catalyst	Rh-VI	Rh-IV	Rh-I	Rh-I	Rh-I	Rh-IA	Rh-II	Rh-IIA	Rh-IIA'	Rh-III
Expt.	124	198	101	104	105	159	202	200	181	183
Temp. °C	74	86	74	75	83	66	85	85	71	71
L (D <sub>2</sub> ) <sup>a</sup>	17.0	9.0	17.0	13.5	20.0	8.8	11.4	9.0	10.5	9.0
L (HC) <sup>b</sup>	0.86	9.9	24	19	28	12	125	198	231	198
1-D <sub>0</sub> <sup>c</sup>	0.016	0.039	0.099	0.030	0.044	0.067	0.034	0.012	0.016	0.067
$\varphi_1$	.00	.052	.047	.037	.032	.286	.298	.32	.46	.373
$\varphi_2$	.24	.146	.185	.268	.243	.304	.281	.19	.23	.334
$\varphi_3$	.14	.130	.155	.223	.176	.120	.137	.13	.12	.110
$\varphi_4$	.12	.130	.158	.137	.135	.085	.100	.08	.08	.072
$\varphi_5$	.32	.328	.305	.231	.266	.116	.126	.12	.12	.083
$\varphi_6$	.03	.034	.034	.029	.032	.026	.017	.03	.00	.009
$\varphi_7$	.04	.033	.026	.020	.025	.022	.014	.03	.00	.007
$\varphi_8$	.03	.038	.029	.022	.026	.015	.012	.03	.00	.005
$\varphi_9$	.02	.039	.026	.015	.025	.011	.008	.02	.00	.003
$\varphi_{10}$	.06	.071	.034	.019	.041	.015	.006	.03	.00	.003
$\Delta^d$	.007	.002	.001	.004	.002	.002	.003	.007	0.07	.002

a) Flow rate of deuterium in cc per min. The ratio of the partial pressure of deuterium to that of cyclopentane was 7.1.

b) Flow rate of cyclopentane in moles per hour per g. of rhodium. c) 1-fraction of unexchanged molecules. d) Uncertainty in fractions of various isotopic species contributed by uncertainty in reading mass spectrometer recordings.

J. A. ROTH, B. GELLER and R. L. BURWELL, JR.

TABLE III. Isotopic Exchange Between Deuterium and Cyclopentane on Palladium, Platinum and Nickel Catalysts

Catalyst <sup>b)</sup>	Pt-I	Pt-II	Pt-III	Pd-III <sup>a)</sup>	Ni-I	Ni-I	Ni-IB
Expt.	213	216	243	47	246	252	254
Temp. °C	55	78	100	60	70	69	70
L (D <sub>2</sub> ) <sup>c)</sup>	14.8	12.0	11.0	10.0	11.2	11.1	11.2
L (HC)	1.24	3.5	1.6	0.031	.077	0.077	0.077
1-D <sub>0</sub>	0.075	0.050	0.007	0.055	.022	0.012	0.022
$\varphi_1$	.281	.273	.23	.082	.096	.12	.178
$\varphi_2$	.121	.149	.06	.062	.222	.20	.269
$\varphi_3$	.102	.091	.10	.027	.128	.15	.134
$\varphi_4$	.105	.086	.08	.044	.078	.10	.079
$\varphi_5$	.327	.314	.20	.139	.098	.10	.083
$\varphi_6$	.019	.021	.02	.005	.031	.03	.028
$\varphi_7$	.012	.016	.05	.020	.033	.04	.025
$\varphi_8$	.013	.018	.05	.057	.047	.03	.027
$\varphi_9$	.010	.015	.06	.113	.051	.05	.047
$\varphi_{10}$	.012	.017	.13	.453	.216	.18	.129
$\Delta$	.001	.002	.01	.001	.004	.008	.004

a) 1.00 g of Pd-III diluted several fold with glass beads. b) Table II gives the meaning of the headings below this. c)  $P_{D_2}/P_{C_5H_{10}} = 7.1$  except = 16 with Pd-III.

Table III gives results of isotopic exchange between cyclopentane and deuterium on palladium, platinum and nickel catalysts. Runs 47 and 254 were initial runs. Runs 213, 216, 243, and 246 were each the second run with cyclopentane. The run preceding 216 at 98° gave a very similar pattern. With Ni-I, several other hydrocarbons were run between runs 246 and 251 but the catalyst was given no regeneration.

**Isotopic exchange between deuterium and various hydrocarbons.** Table IV gives the results of exchange with bicyclo[3.3.0]octane. Rh-I was treated with hydrogen at 200° just before run 110. The run was repeated with very nearly the same results. The next run at 97° exhibited lower activity but the exchange pattern differed only in the values for  $\varphi_9$  to  $\varphi_{14}$  being about twice as great. Three other runs with Pd-III at temperatures between 65 and 75° gave almost identical patterns. In particular,  $\varphi_{11}$  was much lower than  $\varphi_{10}$  and  $\varphi_{12}$  in all. Analysis at parent less C<sub>2</sub>H<sub>4</sub> (*i. e.*, mass 83 and above) showed very similar patterns with equivalent degrees of exchange. A substantial maximum appeared at  $\varphi_6$ . Thus, much of the ethylene which was lost was C<sub>2</sub>H<sub>2</sub>D<sub>2</sub>,

*Isotopic Exchange between Deuterium and Cyclic Hydrocarbons*

TABLE IV. Isotopic Exchange Between Deuterium and Bicyclo [3.3.0]-Octane and Deuterium and 3,3-Dimethylpentane

Cat. <sup>b)</sup>	<i>cis</i> -Bicyclo [3.3.0] Octane					3,3-Dimethylpentane		
	Rh-I	Rh-IA	Pt-II	Ni-I	Pd-III <sup>a)</sup>	Rh-IA	Pt-II	Ni-I
Expt.	110	165	217	249	23	156	220	247
T °C	85	65	68	60	68	120	97	100
L (D <sub>2</sub> ) <sup>c)</sup>	17.3	10.8	10.7	12.0	21.5	9.4	11.7	10.0
L (HC)	11.6	7.2	1.5	0.04	1.1	6.4	1.4	0.03
1-D <sub>0</sub>	0.221	0.079	0.202	0.183	0.066	0.024	0.037	0.012
$\varphi_1$	.090	.305	.421	.332	.027	.316	.695	.184
$\varphi_2$	.176	.270	.155	.319	.055	.094	.085	.085
$\varphi_3$	.111	.078	.063	.077	.041	.125	.085	.415
$\varphi_4$	.106	.080	.050	.072	.018	.131	.062	.192
$\varphi_5$	.108	.053	.042	.058	.023	.313	.067	.124
$\varphi_6$	.111	.043	.043	.025	.046	.014	.007	.000
$\varphi_7$	.100	.039	.058	.021	.082	.000	.000	
$\varphi_8$	.128	.057	.129	.038	.221			
$\varphi_9$	.022	.008	.013	.011	.050			
$\varphi_{10}$	.012	.010	.010	.012	.064			
$\varphi_{11}$	.010	.012	.006	.008	.018			
$\varphi_{12}$	.006	.014	.004	.007	.046			
$\varphi_{13}$	.010	.018	.004	.009	.082			
$\varphi_{14}$	.009	.010	0.03	.009	.221			
$\Delta$	.001	.004	.001	.001	.007	.005	.003	.008

a) 0.170 g of Pd-III diluted with glass beads. b) Table II gives the meanings of headings below this. c) The ratios of the partial pressures of deuterium to hydrocarbon were 15 except that in runs 220 and 247 it was 17.5.

whence bicyclo-octane- $d_8$  had its deuterium atoms distributed on both rings and, in fact, with one deuterium atom on each carbon atom.

Table IV also gives isotopic exchange patterns obtained for 3,3-dimethylpentane. These were determined to assess the severities of concentration gradients in the pores of the catalysts. Run 153 on Rh-I at 110° was very similar to run 156. Run 157 at 130° showed small amounts of  $d_7$ - $d_{13}$ . Mass spectrographic analysis was based on the parent minus methyl peaks.

Table V gives results with bicyclo[3.2.1]octane. In runs 114 and 115 on Rh-I at 93 and 99° and at lower conversions, 0.008 and 0.014, patterns were similar except that  $\varphi_3$  was larger and no species more exchanged than  $d_5$  were observed. Runs 117 and 119 at 124 and 141° on a catalyst whose activity

J. A. ROTH, B. GELLER and R. L. BURWELL, JR.

TABLE V. Isotopic Exchange Between Deuterium and Bicyclo [3.2.1] Octane

Cat. <sup>b)</sup>	Rh-I	Rh-IA	Pt-II	Ni-I	Pd-III <sup>a)</sup>	Pd-III <sup>d)</sup>
Expt.	116	162	226	248	41	48
T °C	110	81	61	70	83	60
L (D <sub>2</sub> ) <sup>c)</sup>	14.0	9.4	10.0	11.4	5.6	15.6
L (HC)	6.7	4.5	1.0	0.027	0.40	0.026
1-D <sub>0</sub>	0.038	0.011	0.019	.185	.052	.643
$\varphi_1$	.293	.361	.760	.414	.478	.189
$\varphi_2$	.557	.492	.120	.512	.284	.160
$\varphi_3$	.072	.075	.061	.044	.108	.103
$\varphi_4$	.026	.033	.035	.015	.029	.0578
$\varphi_5$	.017	.020	.018	.010	.089	.0563
$\varphi_6$	.015	.020	.006	.001	.012	.0351
$\varphi_7$	.002	.000	.000	.001	.002	.0202
$\varphi_8$	.009			.002	.000	.0123
$\varphi_9$	.009			.000		.0046
$\Delta$	.004	.003	.002	.001	.001	.0002

a) 0.025 g of Pd-III diluted with glass beads. b) Table II gives the meanings of headings below this. c) The ratio of partial pressures of deuterium to hydrocarbon was 21 except that in runs 41 and 48 it was 28 and 30. d) 1.0 g. of Pd-III diluted with glass beads.  $\varphi_{10}$  .0027,  $\varphi_{11}$  .0012,  $\varphi_{12}$  .0008,  $\varphi_{13}$  .0004,  $\varphi_{14}$  .0002. This run was preceded by run 47 in Table II and followed by a duplicate run on cyclopentane. Between runs 47 and 49 there was a small loss in activity; 1-D<sub>0</sub> in run 49 was 0.031.

was decaying were, nevertheless, similar to run 116. Several other runs on Pd-III at 60 to 95° closely resembled run 41.

We have analysed the peaks resulting from loss of ethylene in the mass spectrum of bicyclo[3.2.1]octane exchanged on Pd-III. In the sequence bicyclo[2.2.1]heptane, bicyclo[3.2.1]octane, bicyclo[3.3.1]nonane, the ratio of the intensities of parent less ethylene to parent decreases from much larger than unity to about unity. This suggests that most of the ethylene in bicyclo[3.2.1]octane is lost from the cyclopentane ring as one would expect from the greater stability of secondary free radicals and carbonium ions. The accuracy of the analysis is reduced by the large value of minus ethyl, 83% of minus ethylene. Run 40 at 95° on Pd-III gave  $d_0$  0.925,  $d_1$  0.0362,  $d_2$  0.0279,  $d_3$  .0077,  $d_4$  0.0022 and  $d_5$  0.0058 upon analysis of the parent peaks. Analysis at parent minus ethylene gave one major difference, 90% loss of  $d_2$  with

## Isotopic Exchange between Deuterium and Cyclic Hydrocarbons



a corresponding increase in  $d_0$ . Thus, about one-third of the molecules exchanged were doubly exchanged on the ethylene unit of the bicyclo-octane; exchange to  $d_5$  did not involve the ethylene unit. The rather stable delocalized allylic carbanion<sup>13)</sup> derived by loss of a proton from bicyclo[3.2.1]octadiene seems to play no significant role in exchange on palladium.

The runs on rhodium all show a large maximum at  $\varphi_2$ . Similar mass

TABLE VI. Isotopic Exchange Between Deuterium and Bicyclo [3.3.1] Nonane

Cat. <sup>b)</sup>	Rh-IA	Pt-II	Ni-I	Pd-III <sup>a)</sup>
Expt.	167	221	250	25
T °C	65	58	60	60
L (D <sub>2</sub> ) <sup>c)</sup>	10.5	11.5	14.5	3.9
L (HC)	1.4	0.32	0.009	.007
1-D <sub>0</sub>	0.036	.188	.094	.154
$\varphi_1$	.414	.622	.267	.165
$\varphi_2$	.149	.114	.197	.009
$\varphi_3$	.119	.066	.215	.044
$\varphi_4$	.058	.042	.133	.040
$\varphi_5$	.061	.032	.096	.058
$\varphi_6$	.037	.024	.020	.050
$\varphi_7$	.034	.022	.020	.076
$\varphi_8$	.049	.049	.034	.254
$\varphi_9$	.015	.012	.006	.046
$\varphi_{10}$	.014	.0069	.006	.176
$\varphi_{11}$	.007	.0046	.006	.018
$\varphi_{12}$	.007	.0023	.000	.052
$\varphi_{13}$	.003	.0016	.000	.007
$\varphi_{14}$	.032	.0013	.000	.004
$\bar{d}$	.004	.001	.004	.001

a) 0.170 g of Pd-III diluted with glass beads. b) Table II gives the meanings of heading below this. c) The ratios of partial pressures of deuterium to bicyclo-nonane were 75 except that in run 25 it was 158.

J. A. ROTH, B. GELLER and R. L. BURWELL, JR.

spectrometric analysis indicates that most of the dideutero product results from exchange in the ethylene bridge and to a distinctly greater degree than on palladium.

Table VI presents the results of exchange of bicyclo[3.3.1]nonane. Analysis of run 25 on Pd-III at parent less ethylene gave an intensity of  $d_6$  about equal to that at  $d_8$  on the parent,  $d_7$  and  $d_8$  were about equal and their sum was about equal to that of  $d_{10}$  on the parent,  $d_9$  was about equal to  $d_{12}$

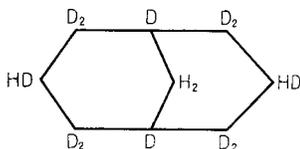
TABLE VII. Isotopic Exchange Between Deuterium and Cyclopentylcyclopentane

Cat. <sup>b)</sup>	Rh-I	Pt-II	Ni-II	Pd-III <sup>a)</sup>
Expt.	109	227	256	36
T °C	84	72	70	60
L (D <sub>2</sub> ) <sup>c)</sup>	15.0	10.8	12.4	10.0
L (HC)	1.0	0.13	0.004	0.022
1-D <sub>o</sub>	0.203	.072	.441	.193
$\varphi_1$	.103	.247	.149	.074
$\varphi_2$	.246	.182	.301	.155
$\varphi_3$	.095	.111	.104	.064
$\varphi_4$	.081	.127	.092	.057
$\varphi_5$	.063	.088	.054	.028
$\varphi_6$	.047	.024	.048	.027
$\varphi_7$	.041	.024	.036	.018
$\varphi_8$	.039	.024	.032	.019
$\varphi_9$	.045	.024	.028	.013
$\varphi_{10}$	.059	.052	.029	.024
$\varphi_{11}$	.027	.014	.019	.010
$\varphi_{12}$	.024	.008	.018	.012
$\varphi_{13}$	.024	.014	.014	.016
$\varphi_{14}$	.023	.014	.015	.017
$\varphi_{15}$	.020	.011	.014	.018
$\varphi_{16}$	.020	.011	.016	.032
$\varphi_{17}$	.017	.011	.018	.060
$\varphi_{18}$	.029	.014	.015	.357
$\Delta$	.003	.004	.001	.002

a) 0.100 g of Pd-III diluted with glass beads. b) Table II gives the meanings of headings below this. c) The ratio of deuterium to hydrocarbon was 150 in run 109, 174 in runs 227 and 256, and 227 in run 36.

*Isotopic Exchange between Deuterium and Cyclic Hydrocarbons*

on the parent. Thus, in exchanged bicyclononane,  $d_8$  involves one deuterium atom on every carbon atom except that of the methylene bridge and  $d_{12}$  is



A preceding run on Rh-IA at 80° to a much higher conversion, 0.36, showed the essential features of run 167, particularly, the maxima at  $\varphi_8$  and  $\varphi_{14}$ . In this run detectable values of  $\varphi_{15}$  and  $\varphi_{16}$  appeared, 0.009 and 0.004.

A run with bicyclo[2.2.1]heptane at 80° on 0.025 g of Pd-III, [ $L(D_2)$  = 4.4 cc per min,  $L(HC)$  = 0.56 moles per g of Pd, ratio of partial pressure of deuterium to hydrocarbon = 16] gave  $D_1$  = 0.17%,  $D_2$  = 1.40% and  $D_3$  = 0.02%. Here, as in other cases, the accuracy in the mass spectrometric determination of  $D_1$  is reduced because of the large correction for  $C^{13}$  in parent plus one.

Table VII presents the results of exchange of cyclopentylcyclopentane. Because of their high boiling points, we were forced to use partial pressures of bicyclononane and cyclopentylcyclopentane which were much lower than in runs with other hydrocarbons.

### Discussion

**Cyclopentane.** The results of isotopic tracer reactions with hydrocarbons can provide a large information content. Thus, one experiment with cyclopentane provides ten items of information which may be taken as the total fraction of cyclopentane exchanged and nine of the ten  $\varphi_i$ , the fractions of each isotopically exchanged species in the product. From an examination of the exchange of cyclopentane on a series of palladium-alumina catalysts,<sup>11)</sup> we concluded that there were uncorrelated variations in the values of at least five of the  $\varphi_i$ 's and that, therefore, there must be at least five different kinds of effective active sites on these catalysts.

Examination of Table II indicates that more than one kind of process occurs on rhodium catalysts. For the most part, rhodium differs from palladium in that  $\varphi_6$ - $\varphi_{10}$  are all small. Contrast, for example, run 105 in Table II with run 47 in Table III. However, the value of  $\varphi_6$ - $\varphi_{10}$  varies considerably on the rhodium catalysts, Rh-IV giving the largest value and Rh-III the least. The relative size of the maximum at  $\varphi_5$  parallels the value of  $\varphi_6$ - $\varphi_{10}$ . Further, in the runs entered at the left of Table II, the ratio  $\varphi_1/\varphi_2$  is small; in those at the right, it is greater than one. However, this ratio does not exactly

J. A. ROTH, B. GELLER and R. L. BURWELL, JR.

parallel yield in cyclopentane- $d_6$ - $d_{10}$ . Compare runs 105 and 159. Thus, there is evidence that at least three uncorrelated processes occur on rhodium catalysts and that there must be at least three kinds of active sites.

One would expect that crystallites of rhodium would be largest for rhodium films (Rh-VI) and for rhodium in the very large pore Filtros (Rh-IV). These catalysts give the largest values for  $\varphi_5$ . This suggests that the progress of reaction (3) and (-3) may require several contiguous sites, a situation more likely to occur on larger crystallites. Table II provides a fair correlation between the relative size of the maximum at  $\varphi_5$  and expected particle size. A nickel-silica catalyst has previously been reported to exhibit increased multiple exchange with increased particle size.<sup>14)</sup>

ANDERSON and KEMBALL<sup>15)</sup> examined the exchange on evaporated rhodium film at  $-85^\circ$ . The isotopic distribution pattern was of the type of Rh-III but the temperatures are too widely separated to permit any very secure comparison. However, their work, as does ours, shows that rhodium is the most active metal of the group which we investigated.

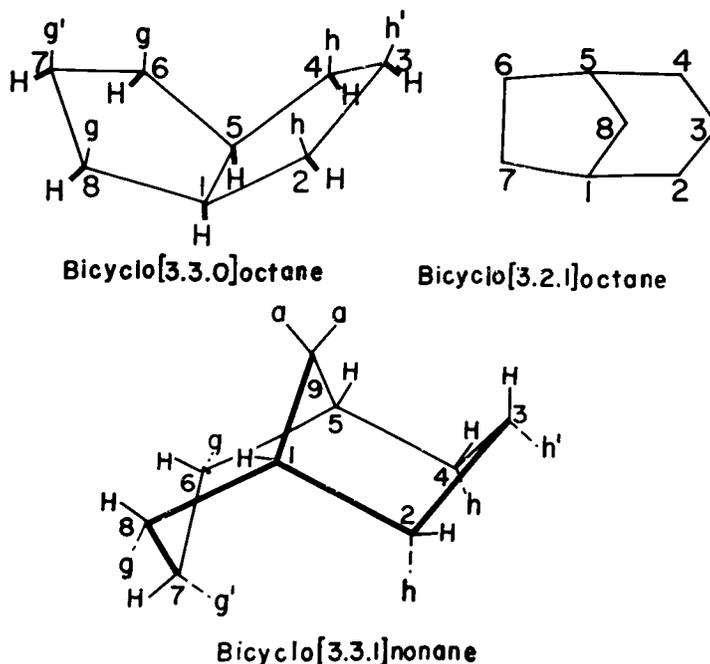
Alumina impregnated with potassium chloroplatinate (Pt-I) gave almost the same isotopic distribution pattern as alumina impregnated with diaminodinitroplatinum (IV) (Pt-II). Relatively, however, silica impregnated with the latter compound gave about five times as much exchange beyond cyclopentane- $d_5$ . In our hands, the use of alumina as a support led to an activity much larger than with silica. Several attempts failed to produce a catalyst more active than Pt-III.

Results on the commercial nickel catalyst differed appreciably from a former run on another nickel-silica catalyst<sup>14)</sup> in showing much more multiple exchange. In the previous run,  $\varphi_2$  was a maximum as in the runs reported here, but beyond  $\varphi_2$  relative exchange declined monotonically although a substantial break followed  $\varphi_5$ . In particular, there was no maximum at  $\varphi_{10}$ .

It appears likely then, that at least two independent processes occur on platinum and nickel catalysts.

**Cis-Bicyclo [3.3.0] Octane.** Let us separately identify the hydrogen atoms on each side of the cyclopentane ring thus:  $C_5H_5h_5$ . Reactions (1), (2) and (3) provide exchange within but one of these sets during each period of residence on the catalyst surface. As shown in Figure 3, we designate the sets in bicyclo [3.3.0] octane as  $C_8H_8(h_2h')$  ( $g_2g'$ ) leaving open the question as to whether h and h' (or g and g') constitute separate sets. If the molecule adsorbs initially in the h- or g-set we might expect to see a maximum at  $\varphi_3$  as is indeed the case with palladium. The nature of the patterns on the other metals is such that this maximum might well be obscured. If initial adsorp-

*Isotopic Exchange between Deuterium and Cyclic Hydrocarbons*



**Fig. 3.** Sets of hydrogen atoms and numbering of bicycloalkanes.

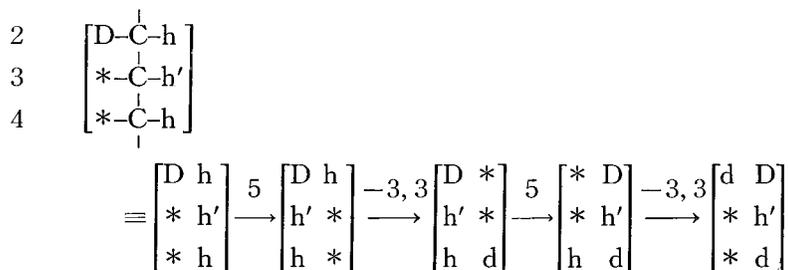
tion occurs into the H-set an unobscurable maximum should appear at  $\varphi_8$ . This is marked on all catalysts as shown in Table IV. Except with palladium, little exchange occurs beyond cyclo-octane- $d_8$ , *i. e.*, two- or three-set exchange is prominent only on palladium.

The results on palladium are of the greatest interest because the greater contrast between small and large peaks discloses more detail. In all runs on palladium  $\varphi_8$  and  $\varphi_{14}$  were about equal and there was a small maximum at  $\varphi_{10}$ .

Bicyclo[3.3.0]octane has a special stereochemical feature which led us to investigate it. It cannot epimerize at just one carbon atom like methylcyclopentane, for example. In bicyclo-octane, epimerization at just one center would lead to *trans*-bicyclo[3.3.0]octane which is so strained that negligible amounts exist in equilibrium with the *cis*-form. The roll-over reaction (5) necessarily inverts the configurations at both carbon atoms attached to the surface. Since roll-over of 1,2-diadsorbed *cis*-bicyclo[3.3.0]octane would give 1,2-diadsorbed *trans*-bicyclo[3.3.0]octane, the process has low probability. Roll-over of 2,3-diadsorbed *cis*-bicyclo[3.3.0]octane should pose no problem but, as shown below, it can never exchange the h' (or g') atom. We show one of the trimethylene bridges.

J. A. ROTH, B. GELLER, and R. L. BURWELL, JR.

carbon



The starting species is diadsorbed in the H-set and all atoms in the H-set have been exchanged by reactions (3) and (-3). The symbolism is shown by writing the starting species in two forms. Thus, no combination of reactions (3) and (-3) and roll-over (Figure 2, reaction (5)) can exchange the h' atom at carbon-2. As with bicyclo[3.3.1]nonane,<sup>3)</sup> this combination of reactions predicts that one should observe maxima at  $\varphi_{10}$  and  $\varphi_{12}$  but that  $\varphi_{13}$  and  $\varphi_{14}$  should be zero. Palladium does show a maximum at  $\varphi_{10}$  which could result from roll-over but the large maximum at  $\varphi_{14}$  cannot.

Roll-over of 1,5-diadsorbed bicyclo[3.3.0]octane by the intermediate of Figure 2 is, of course, impossible sterically. However, this diadsorbed can undergo another form of roll-over mechanism as shown in Figure 4, reaction (6). In this, the 1,5-diadsorbed species rotates so that carbon atoms 8, 1, 2, 4, 5 and 6 enter a plane perpendicular to the surface. This species may be represented as resulting from the interaction of a surface *d*-orbital with a double bond between carbon atoms 1 and 5 and shown in Figure 4 b. Roll-over via the transition state of Figure 4 gives inversion of configuration at both carbon atoms 1 and 5 and leads to 1,5-diadsorbed *cis*-bicyclo[3.3.0]octane in which

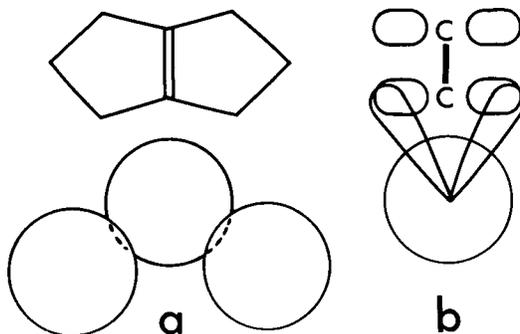
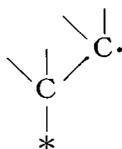


Fig. 4. The transition state in the end-bonded roll-over mechanism. 4 b is a view at 90° to that of 4 a.

*Isotopic Exchange between Deuterium and Cyclic Hydrocarbons*

the H-set has been interchanged with  $h_2h'$  and  $g_2g'$ . Continuation of the sequence, reactions (3) and  $(-3)$ , then leads to bicyclo[3.3.0]octane- $d_{14}$ .

This end-bonded roll-over species would also lead to racemization of optically active hydrocarbons<sup>4)</sup> and to epimerization. The end-bonded roll-over intermediate is related to an intermediate which was proposed some time ago to explain racemization.<sup>16,17)</sup> However, the possibility of continuing the motion



involved in forming this intermediate so as to form the transition state shown in Figure 4 did not occur to us at that time.

Clearly, the methylene groups adjacent to the double bond (carbon atoms 2 and 8) would seriously interfere with the formation of the species of Figure 4 on a densely packed plane like the (111) plane in cubic close-packed. We imagine the species to be formed on the projecting row of atoms on a (110) face or at an edge. The  $\pi$ -allyl mechanism is also impossible on a (111) plane.<sup>18)</sup> Roll-over of 2,3-diadsorbed bicyclo-octane by the intermediate of Figure 4 would lead to the same isotopic results as that by the intermediate of Figure 2.

Let us now consider the application of the  $\pi$ -allyl mechanism to the exchange of bicyclo[3.3.0]octane. Introduction of allyl into cyclopentane is less favored than into propane because of the  $120^\circ$  bond angles favored in  $sp^2$  hybridization. Models of bicyclo-octane indicate that an allyl at carbon atoms 1, 2, and 3 leads to considerably more strain than at 2, 3, and 4 largely because the former requires the binding about one of the bridgehead carbon atoms to be planar and about the other, tetrahedral. If  $\pi$ -allyl is possible only at 2, 3, and 4, one gets a maximum at  $\varphi_{10}$  as with roll-over and as observed on palladium. To get a maximum at  $\varphi_{14}$ ,  $\pi$ -allyl at 1, 2, and 3 is required. It appears highly strained and one would need to assume two kinds of sites each favoring a different  $\pi$ -allylic species. One could evade the problem of strain only by the assumption that an increase in strain energy is fully compensated by an increase in binding energy.

The values of  $\varphi_9-\varphi_{14}$  are too small with rhodium, platinum and nickel to provide much discrimination among possible mechanism of multiset exchange.

**Bicyclo [3.3.1] Nonane.** Like palladium,<sup>3,8)</sup> rhodium, platinum and nickel give maxima at  $\varphi_8$ . Since, in reaction (3), this requires a diadsorbed species at the bridge head and since bridgehead bicyclonene is seriously strained,

J. A. ROTH, B. GELLER and R. L. BURWELL, JR.

we interpret a maximum at  $\varphi_8^{3,8)}$  as indicating that a diadsorbed alkane does not involve a planar disposition about the two carbon atoms attached to the surface as would appear in an extreme form of a  $\pi$ -complexed olefin. It is, of course, quite possible that diadsorbed alkane represents a somewhat variable species intermediate between simple diadsorbed alkane and the  $\pi$ -complex<sup>2)</sup>.

Platinum and nickel, unlike palladium, lead to little material more exchanged than  $d_8$ . Rhodium, however, gives a small but definite maximum at bicyclononane- $d_{14}$ . Neither rhodium, platinum, nor nickel give the maxima at  $\varphi_{10}$  and  $\varphi_{12}$  which are characteristic of palladium. The maxima at  $\varphi_{10}$  and  $\varphi_{12}$  can be explained both by the  $\pi$ -allyl mechanism and by the roll-over mechanism (Figure 2.)<sup>3,8)</sup> Roll-over of 2,3-diadsorbed bicyclononane by Figure 4 would also accord with observations.

**Bicyclo [3.2.1] Octane.** As shown in run 48, Table V, all hydrogen atoms are exchangeable at high conversions on palladium. This was also observed to be true on rhodium. In the initial products, however, palladium, nickel, and platinum give little exchange beyond  $d_5$  and, indeed,  $d_1$  and  $d_2$  constitute an unusually large fraction of exchanged material in all cases. Bicyclo[3.2.1]-octane begins to approach the behavior of bicyclo[2.2.1]heptane in which only two *cis* vicinal hydrogen atoms in one of the ethylene bridges exchange during one period of adsorption as reported in the experimental section. With palladium, rhodium and probably the other metals, much  $d_2$  involves similar exchange in the ethylene bridge of bicyclo[3.2.1]octane. As with bicyclo[3.3.1]nonane and bicyclo[2.2.1]heptane, the methylene bridge cannot exchange with other parts of the molecule in reaction (3) since the bridgehead hydrogen atoms are rigidly held staggered to the hydrogen atoms in the methylene bridges.<sup>4)</sup> The small values of  $\varphi_3$ ,  $\varphi_4$ , and  $\varphi_5$  probably reflect the difficulty in forming *cis*-eclipsed conformations at carbon atoms 2 and 3. Bicyclo[3.2.1]octane is distinctly less flexible than bicyclo[3.3.1]nonane. Further, because of repulsions between the hydrogen atoms at carbon atoms 3 and 7, bicyclononane has a greater tendency to transform into the boat conformation which is necessary for reaction (3).

We are not sure as to the distribution of deuterium atoms in bicyclo-octane- $d_5$ . None are in the ethylene bridge. There are two possible sets of five: 1, 2, 3, 4, 5- $d_5$  and 2, 2, 3, 4, 4- $d_5$  (see Figure 3). The first resembles  $d_8$  in bicyclononane with the ethylene bridge excluded as in bicycloheptane, an exclusion which is strongly suggested by models. In the second possibility, 1,2-diadsorbed must be assumed improbable because of lowered flexibility. However, models suggest that 2,3-diadsorbed is even more strained. Unlike the case with bicyclo[3.3.0]octane, conversion to allyl does not seem unduly

*Isotopic Exchange between Deuterium and Cyclic Hydrocarbons*

disfavored.

As shown in Table V, results with rhodium differ in that exchange progresses to  $d_6$  rather than only to  $d_5$ . We had a number of runs on Rh-I most of which resembled that in the Table. However, two stopped at  $d_5$ . We do not understand these effects nor are we sure where the six deuterium atoms are located. Comparison with the maximum at  $d_{14}$  in bicyclo[3.3.1]nonane suggests that possibly bicyclo[3.2.1]octane-2, 2, 3, 3, 4, 4- $d_6$  is found on rhodium and that the H-, h-, h'-, g- and g'-sets are exchanged on bicyclononane.

**Cyclopentylcyclopentane.** There are three sets of hydrogen atoms in this molecule from the point of view of reaction (3),  $C_{10}H_{10}h_4g_4$  as shown in Figure 5.

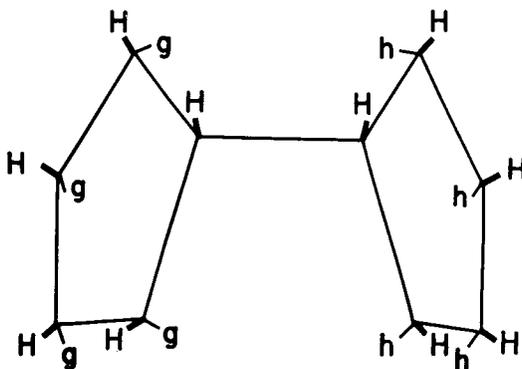


Fig. 5. Sets of hydrogen atoms in cyclopentylcyclopentane.

Initial adsorption into the H-set should result in a maximum or break at  $\varphi_{10}$  and initial adsorption into the h- or the g-sets should show a maximum or break at  $\varphi_4$ . All metals show these.

Suppose that there is some set of surface sites which leads to exchange into more than one set of hydrogen atoms. If a turn-over process or the like is very rapid compared to desorption, all sets could exchange during one period on these sites.<sup>3)</sup> If, however, the turn-over process is comparable in rate to migration from the sites, one would expect to see a break after the exchange of two sets, *i. e.*, after  $d_{14}$ . Palladium shows a large maximum at  $\varphi_{18}$ . The other metals give finite but much smaller values of  $\varphi_{18}$ . No metal shows any break between  $\varphi_{14}$  and  $\varphi_{15}$ . Therefore, processes for multiset exchange must be assumed to be fast on some special set of sites. On other sites, such processes must be very slow since otherwise one would not get a maximum at full exchange of just one set. One possible exception is roll-over (Figure 2) of a 1,1'-diadsorbed cyclopentylcyclopentane upon a protuber-

J. A. ROTH, B. GELLER and R. L. BURWELL, JR.

ance. This would invert the configuration at carbon atoms 1 and 1' and lead to the possibility of forming  $C_{10}D_{18}$  in just one turn-over process.

**Concentration Gradients in Catalyst Pores.** Suppose that diffusional limitations caused the concentration of cyclopentane- $d_5$  to be much higher in the catalyst pores than in the gas phase. We would underestimate the probability that cyclopentane- $d_{10}$  could be formed by exchange of one side, desorption, adsorption, and exchange of the other side. Two sets of data establish that this is not so.

First, consider exchange of cyclopentane on rhodium catalysts shown in Table II. Rhodium gives by far the fastest rates of any metal which we studied. One would expect least  $d_{10}$  on film (Rh-VI) or rhodium in the very large pore Filtros (Rh-IV) and next least in the wide-pore silica (Rh-II and Rh-III) and most on the aluminas. No such correlation is evident. Rather, as we have mentioned, the correlation seems to be most  $d_{10}$  with larger particles of rhodium.

As a further test we examined the exchange of 3,3-dimethylpentane, Table IV.<sup>19)</sup> In one period of residence, no species more exchanged than  $d_5$  can be formed if the rate of formation of  $\alpha, \gamma$ -diadsorbed alkane is of negligible probability and if concentration gradients are negligible. Results accord with this. Exchange of 3,3-dimethylpentane is slow and we had to work at temperatures about 30° higher than with other hydrocarbons. Even so, the run on Rh-IA involves a rather fast exchange and one which is faster than all in Table III.

**Comparison among catalysts.** In the relative values of  $\varphi_1$  in one-set exchange (*i. e.*,  $\varphi_1$  to  $\varphi_5$  for cyclopentane;  $\varphi_1$  to  $\varphi_8$  for bicyclo[3.3.0]octane), platinum and palladium give rather similar results. There is one difference. In bicycloalkanes, platinum-alumina gives relatively much larger yields of  $\varphi_1$  but, even so, the maximum at complete exchange of one set is always substantial. Clearly, on certain sites,  $k_3/k_2$  is small except for cyclopentane and probably cyclopentylcyclopentane. Platinum may be more sensitive to any strain involved in forming an eclipsed diadsorbed species than palladium. On nickel, not only  $\varphi_1$  but also  $\varphi_2$  is relatively much larger on the bicyclic hydrocarbons than on cyclopentane.

The relative degree of exchange beyond one set is always very small on platinum-alumina. Palladium is characterized by an extreme tendency to exchange more than one set. If roll-over mechanisms, Figures 2 and 4, are involved in two-set exchange, the contrast between palladium and platinum may result from relatively weaker binding of diadsorbed alkane (adsorbed olefin) on palladium which correlates with the much greater tendency for the desorp-

*Isotopic Exchange between Deuterium and Cyclic Hydrocarbons*

tion of isomerized olefin during olefin hydrogenation on palladium. If a  $\pi$ -allyl mechanism, Figure 1, is involved in two-set exchange, one needs to assume that palladium exhibits a larger tendency than platinum towards formation of surface  $\pi$ -allyl.<sup>5)</sup>

A platinum-silica catalyst gave much more two-set exchange of cyclopentane (Table III, run 243 *vs.* 216) than did platinum-alumina. Moreover, the platinum-silica catalysts were much less active than platinum-alumina ones although rhodium-silica catalysts were extremely active (Table II).

Nickel-silica catalysts resembled platinum-alumina with two principal exceptions. First, nickel exhibits a tendency for  $\varphi_2$  and  $\varphi_3$  to be relatively large. Second, it possesses sites which lead to considerable two-set exchange of cyclopentane (runs 246, 252 and 254 in Table III) but not with other hydrocarbons (for example, run 249 with bicyclo[3.3.0]octane in Table IV). A different nickel-silica catalyst studied previously<sup>14)</sup> gave much less two-set exchange of cyclopentane.

Rhodium is the most active catalyst for exchange but it gives little two-set exchange particularly at lower temperatures. At about 75°, it usually gives more than platinum but much less than palladium. Rhodium differs from other metals in exchanging to  $d_6$  with bicyclo[3.2.1]octane rather than to  $d_5$ . It differs from palladium in exchanging to  $d_{14}$  with bicyclo[3.3.1]nonane rather than to  $d_{12}$ . We do not know the location of the two additional exchangeable positions. If they are h' and g' at carbon atoms 3 and 7 in Figure 3, it would appear that such two-set exchange as occurs on rhodium proceeds by a mechanism which differs from that on palladium.

The results of exchange on rhodium pose a particular mechanistic problem. Consider run 110 on bicyclo[3.3.0]octane in which  $\varphi_1$  to  $\varphi_8$  are all close to 0.1. As was pointed out some years ago,<sup>20)</sup> one value of  $k_3/k_{-2}$  cannot lead to such a distribution. Nor does the distribution result from diffusional limitations. Rather, it seems likely to result from the presence of a number of sites with different values of  $k_3/k_{-2}$ . Although such heterogeneity is present with all metals, it appears to be extreme with rhodium.

**Conclusion.** The data reported in this paper support the view that the major processes involved in interaction between alkanes and deuterium on palladium, platinum, nickel and rhodium involve dissociative adsorption and associative desorption of alkanes and deuterium, reactions (1) and (2), and the dissociative surface reaction<sup>2)</sup> and its reverse.



The diadsorbed alkane is an  $\alpha$ ,  $\beta$ -diadsorbed species intermediate in geometry

between an eclipsed alkane-like structure and a  $\pi$ -complexed olefin but not very close to the latter. It would appear difficult to specify the structure more closely by present techniques. The value of  $k_3/k_{-2}$  is largest for molecules in which formation of the diadsorbed species is attended by little increase in eclipsing strain (the ratio is larger in cyclopentane than in cyclohexane<sup>3</sup>) and little increase in bond angle strain (with respect to the trimethylene bridge, the ratio is larger in bicyclo[3.3.0]octane than in bicyclo[3.2.1]octane). Sensitivity to the effect of strain seems to be least with palladium.

Hydrogen atoms exchangeable in one period of adsorption by reactions (2) and (3) constitute one set. Maxima or breaks corresponding to complete exchange of one set are always seen in the isotopic distribution patterns except in a few cases in which the maxima or breaks are obscured. All metals studied here give initial products in which more hydrogen atoms have been exchanged than correspond to just one set but only palladium regularly gives substantial yields of two-set or multiset exchange.

Two-set exchange appears to involve sites separate from those which give just one-set exchange. For example, it is difficult to see how two processes on the same set of sites could give maxima at both cyclopentane- $d_5$  and cyclopentane- $d_{10}$  or at cyclopentylcyclopentane- $d_4$ ,  $-d_{10}$  and  $d_{18}$ .

The origin of two-set exchange is still uncertain and possible objections exist to all proposed mechanisms. The roll-over mechanism lacks a close molecular analogy but the following considerations give it some plausibility, particularly on palladium. In the exchange of cyclopentane on palladium,<sup>11</sup> formation of  $d_5$  has an activation energy of 15, of  $d_8$ , 20 and of  $d_{10}$ , 23 kcal. Since the heat of hydrogenation of cyclopentene is 27 kcal, and since isomerized olefin readily desorbs from palladium during the hydrogenation of olefins, a number of surface species equivalent to rather weakly bonded olefin may well be possible.

There are doubts as to the plausibility of the second step of the  $\pi$ -allyl mechanism in Figure 1.<sup>8,11</sup> However the  $\pi$ -allyl mechanism correctly predicts the results of a number of isotopic exchange experiments. Study of isotopic exchange between deuterium and 1-methylbicyclo[3.3.0]octane might distinguish between an end-bonded roll-over and a  $\pi$ -allyl mechanism because 1,2-diadsorbed and, therefore, the end-bonded roll-over mechanisms are impossible. Also, differences in strain energy between the intermediates in  $\pi$ -allyl and roll-over should prove helpful in discriminating between the two mechanisms but, at present, the absence of quantitative relations between strain energy and binding energy prevents any definite decision.

In general, one is inclined to suspect that new types of experimental data

*Isotopic Exchange between Deuterium and Cyclic Hydrocarbons*

may well be necessary for any substantial further mechanistic advances in the field of interaction between hydrocarbons and deuterium on metallic surfaces.

**Acknowledgment.** This work was supported by the Petroleum Research Fund of the American Chemical Society and by the Research Coordination Committee of Northwestern University.

### References

- 1) For a review of this subject through 1960, see G. C. BOND, *Catalysis by Metals*, Academic Press, London, 1962, Chapter 9.
- 2) For a recent partial review, see R. L. BURWELL, JR., *Chem. and Eng. News*, **44**, 56 (Aug. 22, 1966).
- 3) K. SCHRAGE and R. I. BURWELL, JR. J., *Am. Chem. Soc.*, **88**, 4555 (1966).
- 4) R. L. BURWELL, JR., B. K. C. SHIM, and H. C. ROWLINSON, *J. Am. Chem. Soc.*, **79**, 5142 (1957).
- 5) F. C. GAULT, J. J. ROONEY, and C. KEMBALL, *J. Catalysis*, **1**, 255 (1962).
- 6) G. C. BOND and P. B. WELLS, *Advances in Catalysis*, **15**, 91 (1964).
- 7) J. J. ROONEY, *J. Catalysis*, **2**, 53 (1963).
- 8) R. L. BURWELL, JR. and K. SCHRAGE, *Disc. Faraday Soc.*, **41**, 215 (1966).  
See also, general discussion, pp.253-260.
- 9) P. R. STAPP and R. F. KLEINSCHMIDT, *J. Org. Chem.*, **30**, 3006 (1955).
- 10) K. ALDER, H. KRIEGER, and H. WEISS, *Ber.*, **88**, 144 (1955).
- 11) K. SCHRAGE and R. L. BURWELL, JR., *J. Am. Chem. Soc.*, **88**, 4549 (1966).
- 12) This instrument was provided by the National Science Foundation under a matching grant.
- 13) J. M. BROWN, *Chem. Commun.*, 638 (1967).
- 14) R. L. BURWELL, JR. and R. H. TUXWORTH, *J. Phys. Chem.*, **60**, 1043 (1956).
- 15) J. R. ANDERSON and C. KEMBALL, *Proc. Roy. Soc. (London)*, **226 A**, 472 (1954).
- 16) R. L. BURWELL, JR. and W. S. BRIGGS, *J. Am. Chem. Soc.*, **74**, 5096 (1952).
- 17) H. C. ROWLINSON, R. L. BURWELL, JR. and R. H. TUXWORTH, *J. Phys. Chem.*, **59**, 225 (1955).
- 18) Ref. 8, p. 259.
- 19) R. CIOLA and R. L. BURWELL, JR., *J. Phys. Chem.*, **65**, 1158 (1961).
- 20) J. R. ANDERSON and C. KEMBALL, *Proc. Roy. Soc. (London)*, **A, 223** 361 (1954).