JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. *© Copyright, 1966, by the American Chemical Society*

VOLUME 88, NUMBER 20 OCTOBER 20, 1966

Physical and Inorganic Chemistry

Processes of Isotopic Exchange on Palladium Catalysts

Klaus Schrage and Robert L. Burwell, Jr.

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

Abstract: There are at least five distinguishable processes in isotopic exchange between cyclopentane and deuterium on palladium-on-alumina catalysts at 40–70°. One gives mainly cyclopentane-d_{10}, another gives mainly d_8, and a third gives mainly d_5. Two contribute to formation of d_1–d_3. The activation energies for the various processes decrease from about 22 to 11 kcal/mole in the order in which the processes are listed. The kinetic orders in deuterium are about -1.2 for d_8 exchange, -0.85 for d_{10}, a little less negative for d_5, and only about -0.4 for d_1–d_3. The isotopic exchange of methylcyclopentane and 1,1-dimethylcyclopentane can be similarly characterized. Owing to noncorrelated variation in the relative yields of the various cyclopentane-d_i's on different palladium catalysts, each of the five processes is assigned to a different set of surface sites. These results suggest that what appear to be single reactions may, in fact, be composite and more complicated in detail than commonly considered.

Much debate has centered upon whether the surfaces of catalysts and adsorbents are *homogeneous* or *heterogeneous*; that is, do they possess just one kind of active site or several? Most of the discussion has related to chemisorption and support for heterogeneity has predominated.[1] The situation is less clear with respect to catalysis although variation in rate of certain catalytic reactions with crystal face[2a] and results of differential poisoning support heterogeneity. Only in a single crystal work can mere measurement of the rate of a *single* reaction contribute to resolution of the problem.

Isotopic distribution patterns of the products of isotopic exchange between deuterium and cyclopentane and alkylcyclopentanes are unusually rich in detail. In investigating the effect upon these patterns of variation in temperature and in partial pressures of deuterium and hydrocarbon on several palladium-on-alumina and on a rhodium-on-alumina catalyst, we have found what appears to be an unusually powerful tool for determining a minimum number of different types of active sites on these catalysts. It amounts to the simple, simultaneous study of a number of different exchange processes on a series of related catalysts. If from catalyst to catalyst, the rates of two reactions change in a parallel fashion, the two reactions may proceed on the same sites. If the contrary is true, they must proceed on different sites.

There is, of course, an alternative. Each catalyst might contain a single uniform set of sites which differs from catalyst to catalyst so as to give one set of selectivity ratios on one catalyst, another set on another. Presumably, one would need an infinite number of distinguishable sites in this explanation so we shall attempt to apply the former.

In presenting the two alternatives, we assume that concentration gradients in catalyst pores are negligible. As Wheeler showed some years ago, such gradients can alter selectivity ratios. However, the present isotopic exchange reactions are much too slow to cause mass transport effects of this type. Further, the data provide internal evidence against such effects.[2b]

In the present paper we report the details of isotopic exchange between deuterium and cyclopentane and methylcyclopentane, we analyze these into five different processes, and we present evidence to indicate that these processes are each associated with a separate set of sites. In the accompanying paper, paper II,[3] we con-

---

[1] D. O. Hayward and B. M. W. Trapnell, "Chemisorption," 2nd ed, Butterworth & Co., Ltd., London, 1964, pp 212–218.

[2] (a) D. Brennan, *Recent Progr. Surface Sci.*, 2, 57 (1964); (b) R. Ciola and R. L. Burwell, Jr., *J. Phys. Chem.*, 65, 1158 (1961).

[3] K. Schrage and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, 88, 4555 (1966).

sider the implication of these and further data as to the mechanism of these processes.

Experimental Section

Materials. The catalysts were: (I) 0.5% rhodium on alumina, Baker and Co., 40–60 mesh; (II) 0.5% palladium on alumina, Englehard, 60–80 mesh. Both were inhomogeneous because the original pellets had most of the metal toward the exterior. The 5% palladium on alumina was prepared by impregnating Harshaw Chemical Co. γ-alumina with palladium chloride.[4] The alumina was first crushed and sieved to 60–80 mesh. After impregnation, the catalyst was washed, dried in an oven at 110°, and then reduced in hydrogen at 140°. The first batch of this catalyst was used as catalysts III and V. A new batch was used as IV, VI, and VII.

Cyclopentane, Phillips Research Grade, was extracted with 96% sulfuric acid and water, dried over calcium chloride, and distilled from sodium. It was chromatographically pure. Methylcyclopentane, Phillips Research Grade, was used as such. The preparation of 1,1-dimethylcyclopentane has been described.[3] Tank deuterium was obtained from the Liquid Carbonics Division of General Dynamics, San Carlos, Calif. Its isotopic purity was about 99.7%.

Isotopic Exchange Reactions. Reactions were effected in a flow apparatus. Gases were passed through charcoal traps cooled with Dry Ice. The electrolytic hydrogen was first passed through a Deoxo unit (Baker and Co.). The gases were then passed through small rotameters (Fischer and Porter) and thence to a saturator which consisted of a section of tubing filled with Chromosorb P. The Chromosorb was saturated with the hydrocarbon being used and thermostated at that temperature which gave the desired partial pressure of hydrocarbon. Access to the saturator was provided by a stainless steel closure which compressed a copper disk between two raised circular ridges. During filling of the saturator, a funnel containing the hydrocarbon was inserted into the saturator and hydrogen was bubbled through the hydrocarbon to deaerate it. By suitable manipulation, the liquid could be changed without access of oxygen to the catalyst. The gas stream passed from the saturator, over the catalyst, and to a trap in which hydrocarbon was condensed by liquid nitrogen. Fischer and Porter Teflon needle valves were employed instead of stopcocks so as to avoid exposing the catalyst to vapors of stopcock grease.

The rhodium catalyst was treated with flowing hydrogen overnight at 250°. The palladium catalysts were similarly treated at 350°, evacuated for 1 day with a mercury diffusion pump backed by a liquid nitrogen trap, and treated overnight again with hydrogen at 350°. The evacuation and retreatment with hydrogen were omitted with catalysts VI and VII. Runs at reduced partial pressures of deuterium were made by diluting the deuterium flow with a helium one.

After every second or third run, *i.e.*, after about 6 hr on stream, the catalysts were retreated with hydrogen at 350°. Ordinarily the treatment did not affect the catalytic properties detectably. However, during regeneration of catalyst III following run 75, the catalyst was accidentally exposed to air for several hours at 350°. The catalytic activity decreased and the catalytic properties changed. Runs before deactivation are labeled IIIa; after, IIIb.

Deuterium distributions in the product hydrocarbon were determined on a Consolidated 21-130 mass spectrometer provided this department by a matching grant from the National Science Foundation. The ionizing voltage was adjusted individually for each hydrocarbon to optimize accuracy and sensitivity. Particularly with cyclopentane, a broad metastable peak comes at apparent masses *higher* than the parent.[5] This somewhat reduces the accuracy of determining D_2–D_4.

Correction for Isotopic Dilution. The mass spectrometer gives an analysis in terms of D_0, D_1, D_2, etc., where D_i represents the fraction or per cent of the species, alkane-d_i, often shortened to d_i. One would prefer a distribution in terms of the fractions of molecules with none, one, two, etc., hydrogen atoms which had been equilibrated with the surface deuterium–hydrogen pool, *i.e.*, the N_i's.[6] If the fraction of deuterium in the surface deuterium–hydrogen pool is unity, the D_i's and the N_i's are identical. The deuterium content of the pool will be determined by the hydrogen content of the gas phase and by the relative rate of desorption of HD. We assume that the latter reaction is very fast. We have worked at conversions as low as possible and we have converted the observed D_i's into N_i's using the average of the inlet hydrogen content in deuterium (0.003) and the exit content determined from the observed exchange. The difference between the D_i's and the N_i's is substantial only for runs at low pressures of deuterium. Runs with small (run 98) and large (run 97) corrections are given in Table I to exemplify the level of these corrections. The last digit in D_i is significant to about ±5.

Table I. Isotopic Exchange of Cyclopentane on IIIb at 40° ($P_{C_5H_{10}}$ = 110 torr)

	Run IIIb97		Run IIIb98	
L^a	13.8		1.85	
P_{D_2}, torr	80		1390	
P_{He}, torr	560		0	
H/D^b	0.099		0.0065	
	Obsd	Cor^c	Obsd	Cor^c
D_0	0.9733	0.9733	0.9741	0.9740
D_1	0.00256	0.00240	0.00808	0.00808
D_2	0.00382	0.00392	0.00468	0.00470
D_3	0.00156	0.00148	0.00143	0.00143
D_4	0.00217	0.00121	0.00103	0.00094
D_5	0.00712	0.00829	0.00494	0.00505
D_6	0.00009	0.00002	0.00015	0.00014
D_7	0.00057	0.00015	0.00016	0.00015
D_8	0.00197	0.00214	0.00051	0.00051
D_9	0.00181	0.00034	0.00052	0.00032
D_{10}	0.00501	0.00680	0.00433	0.00465

[a] Flow rate of cyclopentane in millimoles per hour. [b] Ratio of hydrogen to deuterium in the exit gas. [c] Corrected for isotopic dilution as described in the text to convert D_i's to N_i's.

In converting D_i to N_i in Table I, we assume that the surface H/D pool is that of the gas phase, *i.e.*, that the rate of desorption of HD is effectively infinite. This may be extreme but one can easily show from many of our runs that the relative rate of desorption of HD is very large. Consider the observed ratio, D_9/D_{10} in run IIIb98 of Table I. If the surface H/D pool is about 0.01 (as against 0.0065 in the gas phase), N_9 is reduced to zero. Thus, 0.01 is an upper limit to H/D in the surface pool and the rate of desorption of HD is at least several hundred times that of exchanged cyclopentane.

Variation in Activity and Selectivity. Activities of the various catalysts in terms of the rate of isotopic exchange between deuterium and cyclopentane are given in Table II. We assume that the reaction is first order in cyclopentane. Then

$$k = L \ln (1/D_0)/w \tag{1}$$

where L is the flow rate of hydrocarbon in millimoles per hour; w is the total catalyst weight in grams, and D_0 is the fraction of hydrocarbon which is unexchanged. The numbers under "Activity" give some notion of the activity of these catalysts although, as will appear, "activity" is not a simple quantity but a composite one.

Table II. Rates of Isotopic Exchange between Deuterium and Cyclopentane at 40°, 100 Torr of Cyclopentane, and 650 Torr of Deuterium

Catalyst		Wt, g	L	D_0	Activity
I	0.5% Rh	0.2	8.3	0.642	18.5
II	0.5% Pd	5	7.1	0.997	0.004
IIIa	5% Pd	15	7.1	0.984	0.008
IIIb	5% Pd	15	5.7	0.987	0.005
IV	5% Pd	15	5.8	0.895	0.045
V	5% Pd	13.5	6.2	0.971	0.013
VI	5% Pd	1.0	6.7	0.991	0.061
VII	5% Pd	0.050		Not determined	

---

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

[5] See C. F. Robinson and L. G. Hall, *Rev. Sci. Instr.*, **27**, 504 (1956).

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

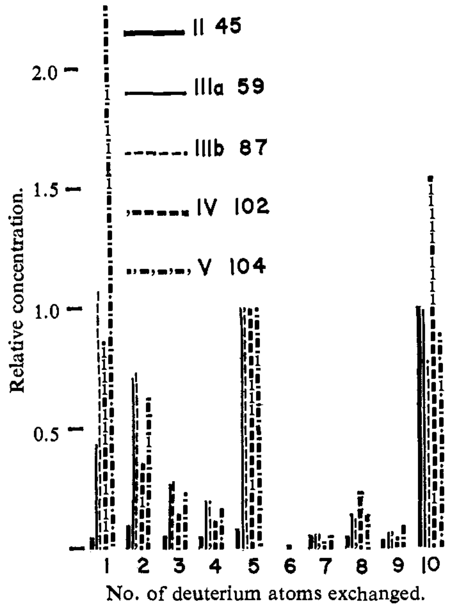

Figure 1. Normalized initial isotopic distribution patterns in the exchange of cyclopentane with deuterium on palladium-on-alumina catalysts at partial pressures of cyclopentane and deuterium of 100 and 650 torr. The temperature was 40° except 50° with run II45. Results are normalized to unity at d_6 except with run 45 which is normalized to unity at d_{10}.

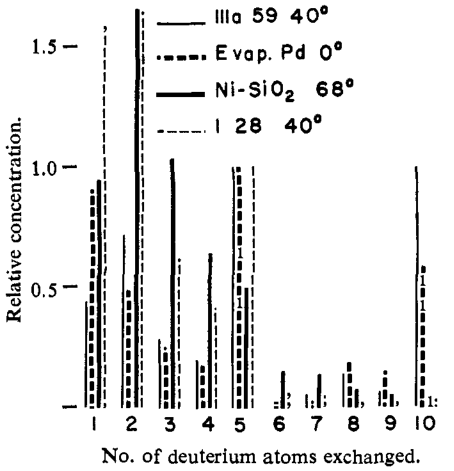

Figure 2. Relative initial isotopic distribution patterns in the exchange of cyclopentane with deuterium on several metallic catalysts. The data have been corrected for isotopic dilution. Evap. Pd is from ref 7, Ni–SiO$_2$ from ref 9.

The catalysts of Table II varied not only in total activity but also in the distribution of the variously deuterated species as shown in Figures 1 and 2. Corrections were made for isotopic dilution here and subsequently. Run V114 which differed from V104 only in replacement of 70 torr of deuterium by helium gave an isotopic distribution pattern like that of V104 except that D_1 was reduced nearly by half, to 1.2. The differences in the patterns of cyclopentane on catalysts III–VI were paralleled by those of methylcyclopentane as may be seen in subsequent figures.

General Results. Figure 3 presents isotopic distribution patterns for cyclopentane on catalyst IIIa as a function of temperature. The distributions are normalized to $D_{10} = 1.00\%$. In the actual runs, total exchange varied from 1.6% at 40° to 16.7% at 70°. Similar trends were found with catalyst II although at any one temperature D_{10}/D_5 is much larger with catalyst II. Figure 4 shows similar data for methylcyclopentane on IIIa.

Normalized runs on catalyst VI are shown in Figures 3 and 4. This catalyst would resemble IIIa rather closely if the temperature of a run on VI was 15° higher than on IIIa (except, of course, that catalyst VI is much more active as shown in Table II). Similarly, catalyst II at temperatures 25–40° lower would resemble catalyst IIIa.

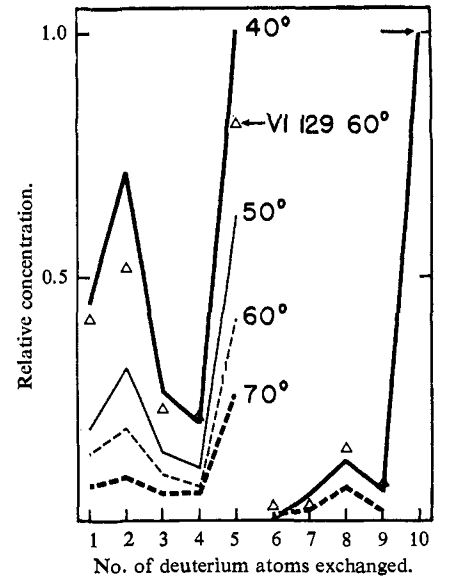

Figure 3. Effect of temperature upon the isotopic exchange of cyclopentane with deuterium; partial pressures of deuterium and cyclopentane, 650 and 100 torr. The runs are for catalyst IIIa except for run 129 on VI. The data are normalized to unity at d_{10}. Actual total per cent exchanged was: run 59, 40°, 1.62; run 60, 50°, 3.49; run 57, 60°, 8.25; run 58, 70°, 16.66; run 129, 4.86. The flow rates in millimoles per hour were 7.1 for cyclopentane and 48.8 for deuterium except in run 129, 6.7 and 47.2.

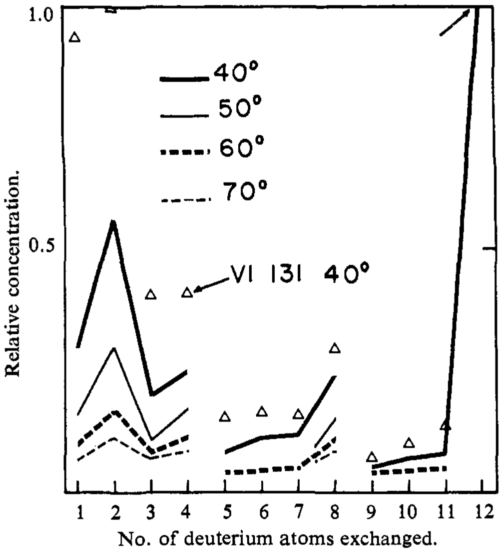

Figure 4. Effect of temperature upon the isotopic exchange of methylcyclopentane with deuterium; partial pressures of deuterium and methylcyclopentane, 670 and 80 torr, except in run 131, 720, and 30 torr. The runs are for catalyst IIIa except for 131 on VI. The data are normalized to unity at d_{12}. Actual total per cent exchange was: run 63, 40°, 1.65; run 64, 50°, 3.68; run 61, 60°, 9.02; run 62, 70°, 18.64; run 131, 2.45. The flow rates in millimoles per hour were 5.9 for cyclopentane and 48.8 for deuterium except in run 131, 1.66 and 39.7.

Figure 5 presents Arrhenius plots of assembled values of D_i's of the unnormalized data from which Figure 3 was derived. The plotted values have been corrected for multiple reaction which was significant at the higher conversion runs at 60 and 70°. For example, with cyclopentane some molecules would undergo reaction leading both to d_2 and to d_{10} with consequent "loss" of d_2. The calculated loss has been added to the observed values. The data of Figure 4 for methylcyclopentane were similarly treated and equally good fits to straight lines were obtained. We plot $-$log

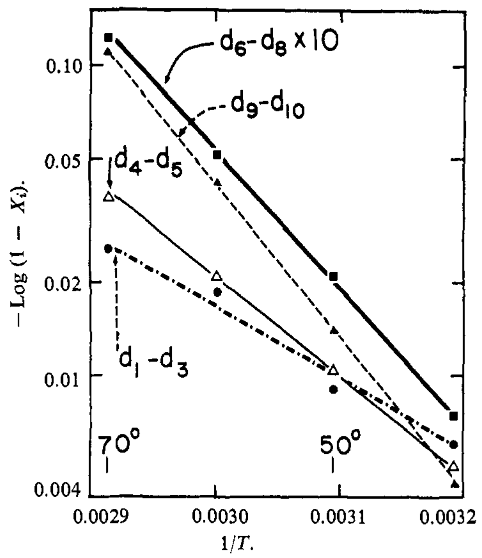

Figure 5. Arrhenius plot of effect of temperature upon the isotopic exchange between cyclopentane and deuterium on catalyst IIIa. Conditions are given in the legend to Figure 3.

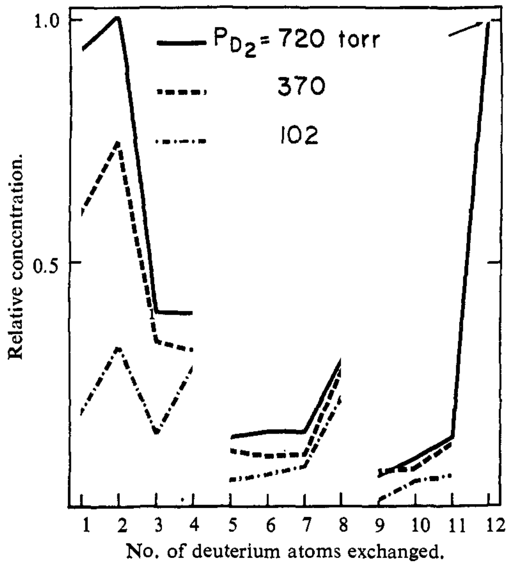

Figure 6. Effect of partial pressure of deuterium upon the isotopic exchange between methylcyclopentane and deuterium at 40° on catalyst VI. The data are normalized to unity at d_{12}. The partial pressure of hydrocarbon was 30 torr. Actual total per cent exchange and flow rate of hydrocarbon were: run 131, 720 torr, 2.41%, 1.66 mmoles/hr; run 132, 370 torr, 2.99%, 2.12 mmoles/hr; run 133, 102 torr, 4.09%, 3.46 mmoles/hr.

$(1 - X_i)$ *vs.* $1/T$ where X_i for cyclopentane represents $(D_1 + D_2 + D_3)$, $(D_4 + D_5)$, $(D_6 + D_7 + D_8)$, $(D_9 + D_{10})$. For methylcyclopentane, X_i is $(D_1 + D_2 + {}^1/_2D_3)$, $({}^1/_2D_3 + D_4)$, $(D_5\text{–}D_8)$, $(D_9\text{–}D_{12})$. Run 57 was on a fresh catalyst. Regeneration preceded run 59 in Figure 5 and runs 61 and 63 with methylcyclopentane. The good straight lines obtained suggest that regeneration had little effect upon activity or selectivity. Derived values of E_a are given in Table III.

Figure 6 exhibits the effect of variation of partial pressure of deuterium at a fixed partial pressure of methylcyclopentane and at a constant temperature, 40°, on catalyst VI. The flow rates were adjusted to restrict the conversion to a few per cent. The distribution patterns are normalized to D_{12} = 1.00. The accuracy of D_9–D_{11} is low because the corrections for isotopic dilution in the very large peak at D_{12} are large fractions of the raw values of D_9–D_{11}. Figure 7 is a similar representation of the effect of deuterium pressure upon exchange patterns of methylcyclopentane on catalyst IIIb. Cyclopentane behaved similarly (see Table I).

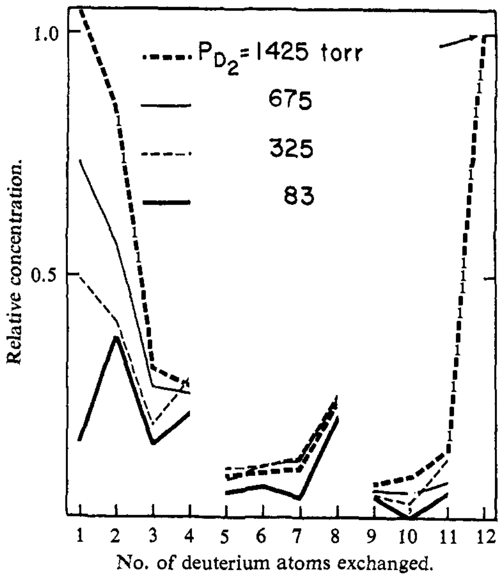

Figure 7. Same as Figure 6 but on catalyst IIIb. The partial pressure of hydrocarbon was 75 torr. Actual total per cent exchange and flow rate of hydrocarbon were: run 99, 1425 torr, 1.82%, 1.99 mmoles/hr; run 88, 675 torr, 1.99%, 2.95 mmoles/hr; run 90, 325 torr, 1.58%, 5.6 mmoles/hr; run 93, 83 torr, 2.38%, 8.9 mmoles/hr.

The assembled, unnormalized values of D_i were converted into rates *via* eq 1 and tested against the equation

$$\text{rate} = kP_{D_2}^{-n} \qquad (2)$$

by plotting log rate *vs.* log P_{D_2}. Values of n are given in Table III. Rather good straight lines were obtained except with D_1–D_3 and the points from the run at P_{D_2} = 83 torr in Figure 7. The values of n for D_1–D_3 were obtained by forced fit.

Table III. Activation Energies and Kinetic Order with Respect to P_{D_2} in Isotopic Exchange of Cyclopentane and Methylcyclopentane

Assembled D_i set		E_a, kcal Catalyst IIIa		Kinetic order in P_{D_2}, $-n$ Catalyst IIIb		VI
C_5H_{10}	C_6H_{12}	C_5H_{10}	C_6H_{12}	C_5H_{10}	C_6H_{12}	C_6H_{12}
D_9–D_{10}	D_9–D_{12}	22.7	21.5	0.85	0.75	0.9
D_6–D_8		20.4	. . .	1.2	. . .	. . .
D_4–D_5	D_5–D_8	14.8	15.2	0.85	0.75	0.7
	D_4–$D_3/2$	. . .	15.2	. . .	0.75	0.7
D_1–D_3	D_1–$D_3/2$	10.5	12.1	←	0.4–0.5[a]	→
D_1–D_{10}	D_1–D_{12}	17.3	18.1			

[a] Poor fit to eq 2. See text.

The effect of varying the partial pressure of hydrocarbon at constant partial pressure of deuterium is smaller than that of the reverse. This was investigated with cyclopentane on catalyst V at 40°: pressure of deuterium, 570 torr; pressure of cyclopentane, 45, 110 (run 114), and 180 torr. The ratios of D_1 and D_6–D_9 to D_{10} were unchanged. The ratio D_5/D_{10} was 1.17 at 45 torr, 1.28 at 110, and 1.51 at 180. D_2–D_4 paralleled D_5.

Discussion

Multiplicity of Different Active Sites. The isotopic distribution patterns of cyclopentane and methylcyclopentane indicate the presence of at least five processes of isotopic exchange and we shall need to consider whether each of these processes is necessarily to be ascribed to a separate set of sites.

As was noted some years ago,[7] both palladium and rhodium catalyze two different processes. One leads to the exchange of a maximum of five hydrogen atoms in cyclopentane, the other to exchange of ten. By symmetry, the five-set of hydrogen atoms must be constituted by those on one side of the cyclopentane ring. By the principles of the introduction to this paper, the two processes occur on different sites since, as shown in Figures 1 and 3, the two processes occur to quite different extents on the different palladium catalysts under equivalent conditions. For example, the ratio D_5/D_{10} increases in the sequence catalyst II, III and IV, and VI. Thus, relative to III and IV, II has a large number of d_{10} sites and VI has a somewhat smaller number.

There is also a process which leads to a maximum at D_8 in the exchange of cyclopentane. We do not believe that this maximum is an artifact because of the systematic variation of D_8 with temperature and partial pressure of deuterium. Since the relative magnitude of the D_8 maximum does not seem to be correlated with any other process of isotopic exchange, we assume that the process occurs on separate sites. However, since the total magnitude of d_8 exchange is small, correlations of d_8 exchange with other processes of exchange is difficult and there is some possibility that it might be associated with the d_5 exchange sites.

Further, the maximum at D_2 in the sequence, D_1, D_2, D_3, which occurs on some catalysts, requires the presence of at least two additional processes.[8] For example, one process could give declining quantities of d_2, d_3, d_4, and d_5, and the other could give mainly d_1. Thus, catalyst V in Figure 1 would have a large number of sites associated with the last process, whereas IIIa would have a small number.

Although the catalyst support may well influence the relative numbers of the different sites which are formed, there is no sign that any type requires the presence of alumina. In Figures 1 and 2, evaporated palladium film[7] closely resembles IV or V in which augmented quantities of d_8 and d_{10} sites are provided (note that the run on evaporated film is at 0°). It seems likely, therefore, that sites on supported and evaporated film catalysts are similar.

As may be seen from Figure 2, any sites giving d_8 and d_{10} exchange on rhodium on alumina are few in number or have a much higher activation energy. Conversion in run 28 was large, 10.4%. Thus, much D_6–D_{10} resulted from two successive adsorptions and not from d_{10} exchange. The few isolated runs which are available for cyclopentane on supported nickel catalysts[9] indicate that the break between D_5 and D_6 shown for one of these runs in Figure 2 is probably real and that nickel shows processes related to d_5 and d_{10} exchange. Interpretation is clouded by the fact that, at lower temperatures on nickel, conversion of monoadsorbed to diadsorbed species (see paper II[3]) is less probable relative to desorption than on palladium and rhodium. Thus, at 60° or so the d_{10} process on nickel gives mainly species of a lower degree of exchange. A similar effect can be seen in exchange of cyclohexane on palladium (see Figure 4 in paper II[3]).

The initial differences among catalysts III–VI appear to originate in the exact details of the original reductions at 140 and 350°. Once reduced, the catalysts were stable even to retreatment with hydrogen at 350°. Only V provided an exception in gradually losing some of its initially very large activity for d_1 exchange. Exposure to oxygen at 350° also effected a substantial change in III as shown in Figure 1 (IIIb *vs.* IIIa): considerable loss in activity except for d_1 exchange.

We have previously observed variations in the isotopic distribution patterns obtained on palladium-on-alumina catalysts,[4] but we did not attempt to interpret these variations in the present fashion. Isotopic distribution patterns resulting from exchange on nickel–silica catalysts[9] vary with the details of reduction in a way which seemed correlated with the particle size of the nickel crystallites formed during reduction. Additionally, we might now consider that some of the sites are associated with incomplete reduction in some of the catalysts. This problem should not appear with palladium catalysts.

General Characteristics of the Exchange Processes. The effect of the temperature and partial pressure of deuterium upon assembled values of D_i for cyclopentane is given in Table III. The assignment of D_4, for example, to a set is arbitrary but, then, D_4 is small. The combination of D_1, D_2, and D_3 may be inappropriate since at least two processes appear to be involved in producing species with this degree of exchange. This is probably reflected in the poor fit of the D_1–D_3 set to eq 2. However, the Arrhenius plots are good.

d_{10} exchange has the highest activation energy and, as previously reported, becomes heavily predominant at temperatures above 100°.[4] Anderson and Kemball[7] reported the activation energy for the over-all process on evaporated palladium film to be 14.2 kcal and they reported 3.0 kcal for what is equivalent to the difference between $d_9 + d_{10}$ exchange and $d_4 + d_5$ exchange. They considered the exchange as resulting from three processes. They did not consider d_8 exchange and they recognized but one process as forming d_1, d_2, and d_3.

All of the exchange processes are inhibited by deuterium but to varying degrees. The most heavily inhibited is the d_8 exchange: $-n = 1.2$. The exchange leading to d_1–d_3 is the least inhibited; $-n$ is about 0.45. Increasing pressure increasingly favors d_1 relatively. Thus, as shown in Table I, at 80 torr of deuterium, D_1 is 11% of total exchange, at 1390 torr, 35%. For formation of d_1, $-n$ is only about 0.3. If one may extrapolate, at pressures of about 100 atm, most of any exchange reaction would occur on the d_1 sites and C_5H_9D would heavily predominate in the initial product.

The effect upon D_1, D_2, and D_3 of these pressure dependencies and the relative numbers of the different kinds of sites may readily be seen. Thus, catalysts VI (Figure 6) and IIIa (Figure 1) exhibit maxima at D_2 throughout our pressure range. They have relatively small numbers of sites giving d_1 *vs.* the number of sites which give d_2. Catalyst V (Figure 1, run 104) has relatively large numbers of d_1 sites, and data we do not report here show that D_1 is a maximum even at 80 torr of deuterium although D_1/D_2 decreases to 1.3

---

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

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

(9) R. L. Burwell, Jr., and R. H. Tuxworth, *ibid.*, **60**, 1043 (1956); R. H. Tuxworth, Doctoral Dissertation, Northwestern University, 1955.

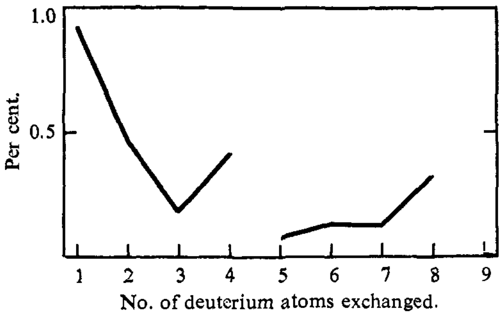

Figure 8. Isotopic exchange between 1,1-dimethylcyclopentane and deuterium on catalyst V, run 122, 45°; partial pressure of hydrocarbon, 42 torr; of deuterium, 708 torr; flow rate of hydrocarbon, 3.2 mmoles/hr.

at 80 torr from 3.6 at 650 torr. Catalyst IIIb is intermediate as shown in Figure 7. D_2 is a maximum at 83 torr but not at 325 torr and higher. Data omitted from Figure 7 show that D_2 is still a maximum at 200 torr.

We have investigated the effect of partial pressure of hydrocarbon upon cyclopentane exchange only in a very cursory fashion. The ratios, D_2–D_4/D_{10} and D_5/D_{10} increase somewhat with increasing partial pressure of hydrocarbon. The ratios, D_1/D_{10} and D_8/D_{10} are unchanged. Previous work[7,10] suggests that kinetic order in hydrocarbon should be unity or slightly less. This, coupled with the negative order in hydrogen, has been taken to mean that coverage by hydrogen is high, by hydrocarbon, low. However, since it is now clear that total exchange is composite and the processes giving extensive multiple exchange are complex, this conclusion may not be firm. For a simple process giving single exchange

$$\mathrm{RH(g)} + 2* \underset{k_3}{\overset{k_{-3}}{\rightleftharpoons}} \mathrm{R{-}*} + \mathrm{H{-}*} \tag{3}$$

$$\mathrm{H_2(g)} + 2* \rightleftharpoons 2\mathrm{H{-}*} \quad K_{\mathrm{eq}} \tag{4}$$

where we assume that hydrogen chemisorption is at equilibrium. For Langmuir–Hinshelwood kinetics, the rate of isotopic exchange would be

$$\text{rate} = \frac{k_{-3}P_{\mathrm{RH}}}{KP_{\mathrm{H_2}}}\left[1 + \frac{k_{-3}P_{\mathrm{RH}}}{k_3KP_{\mathrm{H_2}}} + \left(\frac{1}{KP_{\mathrm{H_2}}}\right)^{1/2}\right]^{-2} \tag{5}$$

The observed value of $-n$ for d_1 exchange of about 0.3 suggests an intermediate degree of hydrogen coverage. If hydrocarbon coverage is small

$$\text{rate} = k_{-3}P_{\mathrm{RH}}\left[\frac{1}{(KP_{\mathrm{H_2}})^{1/2} + 1}\right]^2 \tag{6}$$

Results with methylcyclopentane parallel those with cyclopentane and involve similar activation energies and orders in deuterium. The data of Table III accord with assignment of d_9–d_{12} exchange to the same sites as d_9–d_{10} exchange on cyclopentane. d_5–d_8 exchange and d_4 exchange of methylcyclopentane appear to proceed on the same sites as d_4–d_5 exchange of cyclopentane. Exchange forming d_1–d_3 seems to involve the same sites with both hydrocarbons. However, we cannot identify a reaction of methylcyclopentane on the cyclopentane-d_8 sites. Products of reaction on these sites are probably hidden by products from other sites.

There was some variation among catalysts in details. The ratio of two-set to one-set exchange increased somewhat as the partial pressure of deuterium increased on catalyst V, was hardly changed on catalyst IIIb, and went down on catalyst VI. On the whole, however, the trends with temperature and pressure were remarkably consistent.

Assignment of Sites. Given the existence of at least five processes in cyclopentane exchange and the lack of correlation in their relative rates in a series of catalysts, we have chosen to interpret this as the result of five sites each of which catalyses just one of the processes. Of course, we cannot prove that the situation is not much more complicated. Some of the types of sites might very well catalyze two or more processes. The separation into five discrete types may be too simple; there may be continuous variations between one type and another, and so forth. The basic point, that the surface is distinctly heterogeneous with respect to catalysis, seems to be established. It seems reasonable, at this stage, to employ the simplest interpretation which satisfactorily represents the data.

Judging from the constancy of activation energies and kinetic order in deuterium, the d_{10}, d_8, and d_5 sites are reasonably homogeneous on any one catalyst and rather similar on different catalysts. Since we have not seen how to separate formation of d_1–d_3 or d_1–d_4 into two separate processes, we cannot be sure that the sites involved are homogeneous on the same or on different catalysts. However, similarity in relative changes of D_1, D_2, and D_3 with temperature and pressure of deuterium suggests that sites on different catalysts are not very dissimilar.

We have little information which bears upon the exact topochemical nature of the various sites. Those which represent inate heterogeneity may involve different crystallographic faces, faces of different area, steps and edges, surface point defects, and dislocations. Clearly, we deal with reactions in which the intermediates are surface organometallic complexes. We propose that the nature and reactivity of these complexes will be influenced by the number and stereochemical distribution of palladium atoms linked to a site. Such a view follows almost inevitably from our knowledge as to the effect of the other ligands upon reactivity of the carbon-metal bond in molecular organometallic complexes. Further, the geometric relationship of sites will be of major importance in the formation and reaction of multiply adsorbed organometallic species. In addition, some of the heterogeneity may be induced by adsorption of hydrocarbon residues or perhaps of hydrogen.

These results pose some serious questions with regard to kinetic and mechanistic interpretations of catalytic experiments. How is one to know which of these five sets of sites are active in other exchange reactions on palladium on alumina, in hydrogenation of olefins, in hydrogenation of acetylenes? All of these reactions may be composite processes and the kinetics may be composite as they are for total exchange of cyclopentane in the experiments described here.

Now, the assignment of the sites characterized on cyclopentane to 1,1-dimethylcyclopentane, Figure 8, appears straightforward even including assignment of 1,1-dimethylcyclopentane-d_6 to -d_8 sites. But how is

---

[10] G. C. Bond, "Catalysis by Metals," Academic Press Inc., London, 1962, Chapter 9.

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

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

Acknowledgment. This work was supported by the Petroleum Research Fund of the American Chemical Society, Grant 1579-C.

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

Klaus Schrage and Robert L. Burwell, Jr.

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

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

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

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

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

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

---

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

[2] G. C. Bond, "Catalysis by Metals," Academic Press Inc., London, 1962.

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

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

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

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

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