The pressure-independent (infinite pressure) values of A and E_a should be used in calculations of and comparisons with thermodynamic quantities. The pressure-dependent (low pressure) values of A and E_a are lower in magnitude. It would be helpful to keep this in mind during the following discussion, because many workers did not attempt to determine whether or not their reaction rates were measured in the pressure-independent region.

Kerr and Lloyd have tabulated rate parameters and thermodynamic data for many radical decompositions.[7] Entropies of activation can be estimated from eq xxvi, with the reservations expressed in the preceding paragraph. From the data in Kerr and Lloyd's table we note that, for the decomposition of a large radical RM· into a smaller radical R· and a molecule M that contains a multiple bond, there is a correlation between

$$\mathrm{RM\cdot} \longrightarrow \mathrm{R\cdot} + \mathrm{M} \qquad (24)$$

the identity of R· and the rate parameters A_{24} and E_{24}. When R· is a hydrogen atom, (24) has an activation energy that is within 2 kcal/mol of the thermodynamically calculated endothermic heat of reaction, and the entropy of activation is usually slightly positive [1–4 cal/(deg mol)]. In the cases where the estimated values of $\Delta S_{24}^{\ddagger}$ were negative for R· = H, the reported activation energies were lower than ΔH_{th}; these activation energies are therefore probably lower than the infinite-pressure values, and the corresponding values of A and $\Delta S^{\ddagger}$ would also be low. Increasing $(E_a - \Delta H_{\mathrm{th}})$ to 1 kcal/mol would make $\Delta S^{\ddagger}$ positive in all cases.

When R· is a methyl or ethyl radical the quantity $(E_a - \Delta H_{\mathrm{th}})$ is usually 2–10 kcal/mol and the apparent values of $\Delta S_{24}^{\ddagger}$ are mostly zero or negative.

One cannot have enough confidence in the reported data to know whether the above correlations are significant. However, the most thoroughly studied reactions of these types appear to be (25) and (26),[7] for which $(E_{25} - \Delta H_{25}) = 2$ kcal/mol, $\Delta S_{25}^{\ddagger} = +4$ cal/(deg mol), $(E_{26} - \Delta H_{26}) = 2$ kcal/mol, and $\Delta S_{26}^{\ddagger} = -14$ cal/(deg mol).

$$\mathrm{C_2H_5} \longrightarrow \mathrm{C_2H_4} + \mathrm{H} \qquad (25)$$

$$\mathrm{CH_3CO} \longrightarrow \mathrm{CH_3} + \mathrm{CO} \qquad (26)$$

Our results imply that $(E_7 - \Delta H_7) = 11$ kcal/mol and $\Delta S_7^{\ddagger} = -17$ cal/(deg mol), whereas the corresponding values from the work of Long and Skirrow[5] are 19 kcal/mol and +2 cal/(deg mol). The latter values appear to be too high for that type of reaction.

Reaction between Deuterium and Cyclic Olefins on Platinum/Alumina in the Liquid Phase

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Abstract: This paper reports the results of reaction in the liquid phase between deuterium and cyclopentene, cyclohexene, cycloheptene, cyclooctene, bicyclo[3.3.0]-2-octene, and 1-hexene on platinum/alumina. Runs involved the solvents: none, tetrahydrofuran (THF), THF + D_2O, CH_3COOD, CH_3OD, $(CH_3)_3COD$, and ethanolamine-d_3 + CH_3OD. The exchange reaction, H* + ROD = D* + ROH, proceeds rather rapidly, thus considerably increasing (D*/H*) over the low value which obtains during runs with no solvent or with THF. The increased (D*/H*) facilitates interpretation of the isotopic distributions of the cycloalkanes which are formed. These distributions can now be seen closely to resemble those found in exchange of each cycloalkane with deuterium on platinum, a result which strongly supports the view that exchange of alkanes and hydrogenation of alkenes are closely interlinked mechanistically. The isotopic distributions of cycloalkanes formed in exchanging solvents indicate that there are at least two sets of surface sites. One is characterized by large (D*/H*), some simple addition hydrogenation, all or most of the exchange–addition hydrogenation leading to ane-d_3, ane-d_4, . . . , and a substantial rate of H* + ROD = D* + ROH. The second set involves only or mainly simple addition hydrogenation, formation of exchanged olefin, and a relatively small rate of H* + ROD = D* + ROH. There are differences among the solvents; CH_3COOD gives much the most exchange–addition hydrogenation, ethanolamine gives much the most simple addition hydrogenation.

If one replaces hydrogen by deuterium and analyzes the products mass spectrometrically, one adds considerably to the information about the hydrogenation of olefins on group VIII metals.[1,2] It becomes evident that the reaction is an *exchange–addition* hydrogenation rather than a simple addition hydrogenation; that is, the addition of deuterium atoms to the original double bond is accompanied by exchange of hydrogen atoms of the hydrocarbon. Thus, product alkane is represented not only by alkane-d_2 but also by -d_3, -d_4, and even higher. In terms of the classical Horiuti–Polanyi mechanism of Scheme I,[3] hydro-

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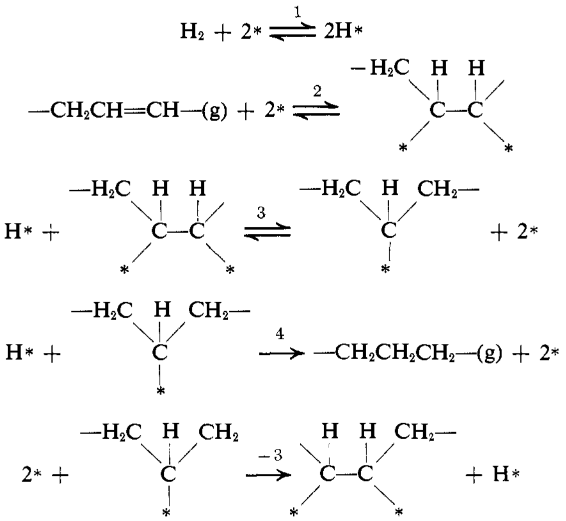
(1) J. Turkevich, F. Bonner, D. O. Schissler, and A. P. Irsa, *Discuss. Faraday Soc.*, **8**, 352 (1950).

(2) G. C. Bond, "Catalysis by Metals," Academic Press, London, 1962, Chapter 11.

(3) R. L. Burwell, Jr., *Accounts Chem. Res.*, **2**, 289 (1969). It has been

Scheme I. The Horiuti–Polanyi Mechanism



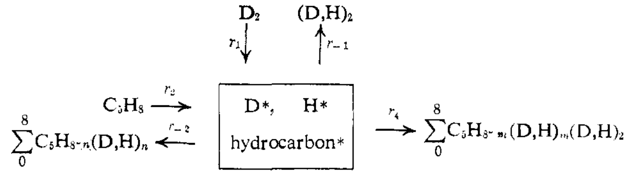
genation does not involve just the once-through sequence, reactions 1, +2, +3, and 4. The rate of reaction −4 is negligible under conventional conditions of hydrogenation[2,3] but, if reaction −3 is rapid enough, alternation between −3 and +3 can provide any degree of alkane exchange. Isomerization of the olefin accompanies hydrogenation, and this has usually been assumed to result from the reversibility of reaction 2 as well as that of 3. Use of deuterium leads to formation of isotopically exchanged olefin. This too has often been ascribed to the reversibility of reactions 2 and 3.

Unfortunately, the interpretation of hydrogenations with deuterium is usually difficult. In the surface hydride pool, (D*,H*), the ratio (D*/H*) is apt to be of the order of magnitude of unity as evidenced by the formation of substantial amounts of alkane-d_0 and -d_1. Thus, H rather than D adds to many positions and information is lost. A marked advantage of the study of isotopic exchange between deuterium and alkanes has been that there (D*/H*) is very large.[3]

Most studies of reaction between hydrocarbons and deuterium have involved reactants in the gas phase. In the present paper, we consider liquid-phase, batch hydrogenations run under conditions close to conventional hydrogenation in the laboratory. We have used platinum/alumina as the catalyst because considerable information is available about its properties and catalytic characteristics and because, since it gives much less double bond migration than most other group VIII metals, results should be simpler and more readily interpreted. Let us, therefore, consider the problem of (D*/H*) in terms of reaction between deuterium and cyclopentene on platinum/alumina. We assume (D*/H*) to be *uniform over the surface* and to result from the processes forming and removing H* and D* shown in Scheme II.

Reaction 1 forms D*. In generating cyclopentane-$(d,h)_m(d,h)_2$ ($\equiv C_5H_{8-m}(D,H)_m(D,H)_2$), no H* results from the addition of two (D,H) atoms to the original double bond position, but formation of $(d,h)_m$ and olefin exchange involve cleavage of C–H bonds to form C* and H*. Surface H* and D* react in the ratio (D/H), which is (D*/H*) corrected for kinetic isotope effects, which we assume to be the same for all reactions removing (D*/H*): reactions −1, 3, and 4.

Scheme II. Reaction between Deuterium and Cyclopentene in Initial Stages[a]



[a] The numbering of reactions appears in Scheme I. (D,H) represents a hydrogen atom which has been equilibrated with the (D*,H*) pool.

Presence of olefin inhibits reaction −1 in gas-phase reactions[4] and in liquid-phase hydrogenations on reduced platinum oxide.[5]

The per cent of cyclopentane-$(d,h)_i$ in total cyclopentane will be represented by N_i, where $i = m + 2$ in $C_5H_{8-m}(D,H)_m(D,H)_2$ and $i = 2, 3, \ldots, 10$. N_0 and N_1 are necessarily zero, since the two (D,H) atoms added to form alkane must be equilibrated with (D*,H*). A particular ane-$(d,h)_i$ appears as a mixture of ane-d_i, -d_{i-1}, -d_{i-2}, . . . in the proportions given by the standard binomial distribution.[5] (D/H) represents the relative probabilities of adding D or H to the positions equilibrated. A given ane-d_i receives contributions not only from $(d,h)_i$ but from all species with more than i positions equilibrated. Given the set of N_i's and (D/H), one can calculate the alkane per cent D_i of each exchanged species ane-d_i.

For mechanistic purposes we need the N_i's, but the mass spectrometer gives us the D_i's. However, on the model described above, one can compute the N_i's and (D/H) from the D_i's. For any particular value of (D/H) within a certain range, one can select values of $N_{10}, N_9, \ldots, N_2$ which reproduce $D_{10}, D_9, \ldots, D_2$. The set of N_i's and (D/H) is correct if the N_i's sum to 1.00 (N_0 and N_1 are necessarily zero) and D_0 and D_1 are correctly given. Only one of the range of values of (D/H) which leads to fits of D_{10}–D_2 leads to a fit to D_0,D_1 and it is this, then, which specifies (D/H) and the N_i's. We have applied this procedure to certain liquid-phase hydrogenations in which (D/H) is relatively large, and a more extended application has been given by Weitkamp.[6] However, (D/H) will be small in most liquid-phase hydrogenations and, as (D/H) decreases, the reliability of the computation decreases rather rapidly.

One might increase the value of (D*/H*) by running the hydrogenation in a deuterated solvent which exchanges with (D*,H*) more rapidly than deuterium gas exchanges with (D*,H*) and which provides a larger store of exchangeable deuterium. We have suggested that certain previous studies which employed acetic acid-*d* might have involved such an effect.[5] Accordingly, in the present paper we have investigated a number of solvent systems from this point of view,

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suggested that diadsorbed alkane at the right of reaction 2 should be written as a π complex to one surface atom of the metal. There is no conclusive evidence as to the exact nature of this species, but the geometry of the hydrocarbon part is closer to alkane than to olefin. From a mechanistic point of view, the two forms are nearly equivalent.

(4) D. D. Eley in "Catalysis," Vol. III, P. H. Emmett, Ed., Reinhold, New York, N. Y., 1955, p 63; J. Erkelens, A. K. Galwey, and C. Kemball, *Proc. Roy. Soc., Ser. A*, 260, 273 (1961).

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

(6) A. W. Weitkamp, *J. Catal.*, 6, 431 (1966).

employing cyclopentene and deuterium on 5% platinum/alumina as the test reaction. Although we did not find solvent systems which keep (D/H) as near infinity as one might hope, we did find solvents which give much increased values of (D/H). Reactions of cyclopentene, cyclohexene, cycloheptene, cyclooctene, *cis*-bicyclo[3.3.0]-2-octene, and 1-hexene were then studied in a selected set of solvent systems.

Experimental Section

Materials. Commercial olefins were purified by preparative gas chromatography. The bicyclo[3.3.0]octene was made by Dr. B. Geller.[7] Olefins were inserted into the reactor *via* percolation through alumina to remove impurities, probably mainly hydroperoxides. Tetrahydrofuran was purified by distillation from potassium metal. It too was percolated through alumina.

2-Aminoethanol-d_3 ($D_2NCH_2CH_2OD$) was prepared from aminoethanol, purified by fractional distillation, and then exchanged with D_2O. Seven successive portions of D_2O were added to the aminoethanol and then, after about 6 hr, distilled off. By nmr analysis, 99% of the three exchangeable hydrogen atoms had been replaced. Methanol-d_1 (CH_3OD) was prepared by hydrolysis of dimethyl carbonate, catalyzed by D_2SO_4.[8] Refluxing 187 ml of dimethyl carbonate, 45 ml of D_2O, and 5.9 ml of dimethyl sulfate under nitrogen gave CH_3OD, whose isotopic purity was 98% by nmr analysis. Acetic acid-d_1 (CH_3COOD) was obtained by refluxing acetic anhydride and D_2O. The isotopic purity was 99%.

tert-Butyl alcohol-d_1 (*tert*-C_4H_9OD) was prepared from alcohol purified by fractional distillation. It was treated with five successive portions of D_2O, and each portion was salted out by addition of potassium fluoride. As judged by nmr analysis in dimethyl sulfoxide,[9] its isotopic purity was 90% and, by refractive index measurement, it contained about 4% water.

All experiments were performed on 5% platinum/alumina, Baker, Lot 2728, crushed and sieved to smaller than 200 mesh.

Analysis. Products were analyzed and separated for mass spectroscopy by gas chromatography. Mass spectrometric analyses were performed on a Consolidated 21–130 mass spectrometer obtained by a matching grant from the National Science Foundation. Reduced ionizing voltages were usually employed.

Apparatus and Technique. Hydrogenations with deuterium were conducted in an agitated batch reactor of the type developed by Hussey.[10] The water-jacketed reactor vessel contained a 10-ml bulb with two creases from which projected a small tube for a serum cap and a larger tube leading to a standard-taper joint. This was connected to the hydrogen or deuterium supply *via* a Tygon tubing and a tube containing Linde 4A sieve. Deuterium (Matheson) was purified by passage through Linde sieve 5A at −78°. It was stored in a 100-ml buret with mercury as the confining fluid, which was part of a constant-pressure system controlled by tungsten leads in a mercury manometer, which led to the actuation of a magnetically controlled solenoid valve positioned between a 5-l. ballast volume, containing air at 100 psi, and the buret bulb. The system pressure was 1 atm in all experiments. The reactor was agitated by being fixed to a 3-mm off-center eccentric attached to a 1750-rpm motor.

Runs were made in the following fashion. A weighed sample of catalyst (5–30 mg) was placed in the apparatus which was then evacuated. The catalyst was exposed to deuterium for 5 min following which the apparatus was evacuated again. Deuterium was reintroduced and the solvent added. The reactor was agitated for 10 min, 10 ml of gas was extracted through the septum cap, the olefin was injected through the septum cap, and the hydrogenation was started.

Compositions of olefin and solvent which were run regularly are given in Table I. Other compositions will be described as needed. Unless otherwise stated, all reaction compositions consisted of 0.1 ml of olefin and 1.5 ml of solvent. Previous work[11] and our examination of tetrahydrofuran indicate that exchange of skeletal hydrogen atoms in the solvents will be much slower than that of OD or ND_2.

Table I. Compositions in Runs

Symbol	Olefin, ml	Solvent, ml
Neat	1.0	None
THF	0.1	Tetrahydrofuran, 1.5
THF–D_2O	0.1	Tetrahydrofuran, 1.5 + D_2O, 0.1
EA	0.1	CH_3OD, 1.0 + $D_2NCH_2CH_2OD$, 0.5
CH_3OD	0.1	CH_3OD, 1.5
AcOD	0.1	CH_3COOD, 1.5

The agitation in the reactor was excellent and mass transport of deuterium or hydrogen from the gas phase to the particles of catalyst was not rate limiting. First, considerable reduction in the revolutions per minute of the motor did not reduce the observed rate in experiments in which hydrogen was adsorbed at 4.5 ml/min. Second, the rate was proportional to the amount of catalyst. In the experiment which tested this, the solvent was *tert*-butyl alcohol, the catalyst weight was varied from 5 to 25 mg, and the rate at 25° with the largest amount of catalyst was 4.3 ml/min.

Most of our runs were stopped at low conversions. However, hydrogenation of cyclopentene to 100% conversion in *tert*-butyl alcohol proceeded at constant rate throughout and, upon injection of a new sample of cyclopentane, hydrogenation was reestablished at the initial rate. This establishes the absence of poisoning.[10] However, in tetrahydrofuran the rate of hydrogenation fell beyond 80% conversion. Presumably, then, we had some poisoning, but our results depend only upon the first few per cent of hydrogenation. Runs in other solvent systems were zero order up to at least 20%, but we did not rigorously test for the degree of poisoning. Rates in the solvent systems of Table I differed little, except EA was much slower, 0.1 or less of the neat. With olefins other than cyclopentene, EA gave rates only about $^1/_{40}$th that of neat olefin, except for cyclohexene, which gave a negligible rate. With cyclohexene, useful rates were achieved only with 0.05 ml of $DOCH_2CH_2ND_2$ + 1.45 ml of CH_3OD.

Isotopic Exchange between Solvent and the Surface Pool (D*,H*). In scanning experiments, we hydrogenated cyclopentene (0.1 ml) with deuterium at 25° to about 80% conversion. We employed 1.5 ml of undeuterated solvent. We assumed that the lower the deuterium content of the resulting cyclopentane, the greater the degree of exchange between solvent and (D*,H*). In general, all solvents containing hydroxyl groups gave low degrees of deuteration in the

Table II. Reaction between Cyclopentene and Deuterium or Hydrogen in *tert*-Butyl Alcohol-d_1 or -d_0 at 24° [a]

Gas:	H_2	D_2	D_2	D_2
Solvent:	*tert*-BuOD	*tert*-BuOD	*tert*-BuOD + D_2O[b]	*tert*-BuOH
	%D			
D_{10}[c]	0.0	0.1	0.2	0.0
D_9	0.0	0.2	0.4	0.0
D_8	0.0	0.4	0.7	0.0
D_7	0.1	0.8	1.5	0.0
D_6	0.4	1.9	2.9	0.0
D_5	1.5	4.6	5.9	0.0
D_4	3.4	8.7	10.0	0.0
D_3	7.2	16.8	18.5	0.6
D_2	20.4	31.7	27.1	3.5
D_1	36.0	25.3	22.2	19.7
D_0	31.0	9.5	10.5	76.2
D_{av}[d]	1.23	2.20	2.41	0.29
Rate[e]	0.15	0.064	0.078	0.15

[a] All runs were to 30% hydrogenation and used 10 mg of catalyst. [b] The solvent was 1.5 ml of *tert*-BuOD + 0.5 ml of D_2O. [c] Per cent of each isotopic species in cyclopentane. [d] Average number of deuterium atoms in the cyclopentane. [e] Rate of hydrogenation in ml of D or H/min per mg of catalyst.

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

(8) A. Streitwieser, Jr., L. Verbit, and P. Stang, *J. Org. Chem.*, **29**, 3706 (1964).

(9) O. L. Chapman and R. W. King, *J. Amer. Chem. Soc.*, **86**, 1256 (1964).

(10) A. S. Hussey, G. W. Keulks, G. P. Nowack, and R H. Baker, *J. Org. Chem.*, 33, 610 (1968).

(11) For example, E. L. McDaniel and H. A. Smith, *Advan. Catal.*, **9**, 76 (1957).

Table III. Effect of Conversion upon Reaction between Deuterium and Cyclopentene in Ethanolamine-d_3 + Methanol-d^a

Run:	S63	S64	S9	S8
Ane, %:[b]	1	9.5	14.0	29.4
	$\%D_i$			
		Cyclopentane		
D_8	0.0	0.0	0.0	0.0
D_7	0.0	0.1	0.1	0.2
D_6	0.0	0.2	0.3	0.6
D_5	1.6	1.3	1.4	1.9
D_4	2.5	2.8	4.2	5.8
D_3	8.2	9.7	15.5	19.8
D_2	67.9	66.3	60.8	56.1
D_1	17.4	18.7	16.6	14.6
D_0	2.4	0.9	1.1	1.0
D_{av}	1.96	2.00	2.11	2.24
		Cyclopentene		
D_5	0.0	0.0	0.1	0.4[c]
D_4	0.0	0.1	0.7	0.9
D_3	Trace	0.5 (0.1)[e]	1.4	2.1
D_2	0.5	2.7 (1.8)[e]	7.2	10.2
D_1	2.2	15.3 (18.5)[e]	27.2	33.4
D_0	97.3	81.4 (79.7)[e]	63.4	52.9
D_{av}	0.03	0.23	0.49	0.66
M^d	2.6	2.1	2.5	1.9

[a] Composition EA of Table I. Temperature of runs was about 26°. About 30 mg of catalyst was employed in each run except in run S64, in which 40 mg was used. [b] Per cent cyclopentane formed. [c] D_6 was 0.1%. [d] M is the ratio of D_{av} in the product to twice the fraction hydrogenated; *i.e.*, $M = (X_{ane}\text{ane-}D_{av} + X_{ene}\text{ene-}D_{av})/2X_{ane}$. [e] Binomial distribution for cyclopentene with D_{av} = 0.23.

Table IV. Isotopic Distributions in Runs with Cyclopentene at about 24°

Run:	S72	S59	S73	D_8	S62	Pt-I[f]
Solvent:[a]	Neat	THF	THF–D_2O	THF–D_2SO_4	CH_3OD	
Ane, %:[b]	10.5	9.7	1.5	8[e]	7.9	
			$\%D_i$			
D_{10}	0.0	0.0	0.0	Trace	0.0	1.2
D_9	0.0	Trace	0.2	0.6	0.1	1.0
D_8	Trace	0.1	0.6	0.9	0.2	1.3
D_7	0.1	0.2	0.9	1.5	0.4	1.2
D_6	0.3	0.4	1.2	2.2	0.8	1.9
D_5	1.4	1.4	6.2	6.3	3.4	32.7
D_4	4.6	3.7	7.9	10.9	6.6	10.5
D_3	9.6	8.1	13.6	14.3	11.6	10.2
D_2	19.9	21.9	37.9	27.0	28.6	12.1
D_1	35.5	38.5	24.0	27.6	32.4	28.1
D_0	28.6	25.7	7.5	8.7	15.9	(0.0)
D_{av}	1.32	1.33	2.23	2.36	1.78	3.40
Ene-D_0	94.4	89.4	96.4	97.0	90.2	0.00
Ene-D_{av}	0.08	0.13	0.05	0.05	0.13	
M^c	1.0	1.3	2.7[d]	1.5[e]	1.7	

[a] From Table I except THF–D_2SO_4 which is 1.5 ml of THF + 0.1 ml of 5% D_2SO_4 in D_2O. [b] Per cent cyclopentane formed. [c] See footnote *d*, Table III. [d] Per cent accuracy is low because of low hydrogenation. In a run at 4.4% hydrogenation, M was 2.9. [e] Accuracy in per cent hydrogenation is low because it is determined only from deuterium consumption. In a run at 30% hydrogenation, M was 2.2. [f] Initial products of isotopic exchange between cyclopentane and deuterium in the gas phase at 55° on 0.42% platinum/alumina from ref 7. In the actual run, D_0 was 95%. Listed values represent the distribution of the exchanged material.

cyclopentane. On the basis of this work, the solvent systems of Table I were chosen.

These experiments were extended in runs with *tert*-butyl alcohol, as shown in Table II. An additional run using deuterium and *tert*-butyl alochol-*d* which contained 5 vol % D_2SO_4 gave results close to those of runs without the sulfuric acid.

Reactions between Deuterium and Various Olefins. Formation of isotopically exchanged cyclopentene accompanied that of cyclopentane in runs. Subsequent hydrogenation of the exchanged cyclopentene distorts the isotopic exchange pattern of cyclopentane from that observed initially. This is exemplified for EA ($DOCH_2CH_2ND_2$ + CH_3OD) in Table III. In these runs, the solvent contained about 50 mmol of deuterium atoms. The gas volume of the reactor, about 20 ml, contained about 1.7 mmol of deuterium atoms. In the run at highest conversion, S8, 0.71 mmol of hydrogen atoms was transferred to solvent and gas phase. Thus, contribution of progressive isotopic dilution to the distortion of the initial isotopic distribution pattern of cyclopentane is minor.

Table IV presents results of reactions between deuterium and cyclopentene in various solvent systems, to which Table V adds results in acetic acid-*d*. Dioxane gave results like THF. THF–1% D_2SO_4 was like THF–5% D_2SO_4.[12] Table VI gives results in THE–5% D_2SO_4 at 3.6.

Tables VII and VIII present results with 1-hexene, cyclohexene cycloheptene, cyclooctene, and bicyclooctene in the solvent systems EA and AcOD (Table I). Runs were also made in the other solvent systems of Table I. Runs in THF–D_2O are of the same type as those in AcOD and these two solvents gave the largest values of ane-D_{av} and M. However, except for cyclooctene, quantities of the more highly exchanged species were somewhat smaller in THF–D_2O, much as in run S73 (Table IV) *vs.* run S65 (Table V). Runs in CH_3OD had still lower values of the more exchanged alkanes and larger values of $D_0 + D_1$, much like run S62 *vs.* run S73 in Table IV. Similar parallels were observed for runs in THF and neat.

Olefin Exchange. The isotopic distribution of recovered cyclopentene for solvent system EA, shown in Table III, results mainly from single-atom exchange, but there are substantial contributions from many-atom exchange. The distribution of cyclopentene in run S59 (THF) in Table IV is of the same general type: D_0 = 89.4, D_1 = 8.5, D_2 = 1.6, D_3 = 0.4, and D_4 = 0.1%. Similarly, the pattern for ene-D_1 in run S61, THF–D_2O, is D_0 = 87.3, D_1 = 9.7, D_2 = 2.0, D_3 = 0.7, D_4 = 0.2, and D_5 = 0.1%. The per cent hydrogenated was 4.4 and the distribution in ane-D_i was nearly identical with that in run S73, Table IV. Most distributions were of this type except for those from runs in AcOD (Table V), which involved more many-atom exchange. It should be remembered that the observed distributions are not the "true" ones, since the olefin has exchanged with a pool in which (D*/H*) is not infinite.

Discussion

The solvent systems of Table I which contain OD groups all lead to substantial increases in (D*/H*) and (D/H) [(D/H) is (D*/H*) corrected for kinetic isotope effects] and to a much closer approach of ane-D_i's

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[12] In attempts to study THF + D_2O + NaOD, even very small amounts of NaOD led to agglomeration of the catalyst.

Table V. Isotopic Distribution of Cyclopentane in Run S65 in CH_3COOD at 24.6°, 2.6% Hydrogenation

		A		B		C		
i	D_i (obsd)	D_i,[a] %	N_i, %	D_i,[b] %	N_i, %	N_i,[c] %	N_2', %	ene-D_i,[e] %
10	0.0	0.06	0.4	0.07	0.2	0.2	0.0	
9	0.4	0.35	1.4	0.4	0.8	0.8	0.0	
8	1.4	1.4	4.0	1.4	2.4	2.4	0.0	
7	1.7	1.9	0.0	1.7	1.3	1.3	0.0	
6	2.1	2.1	2.5	2.1	2.3	2.3	0.0	0.0
5	13.8	13.8	33.0	13.8	21.5	21.5	0.0	0.1
4	15.0	15.0	1.9	15.0	11.7	11.7	0.0	0.2
3	15.4	15.4	15.6	15.4	14.3	14.3	0.0	0.8
2	26.9	26.9	29.3	26.9	27.9	22.2	23.3	1.1
1	15.9	10.1		5.4				2.0
0	7.4	1.1		0.3				95.8
D_{av}	2.84[d]							0.08
(D/H)[f]			$\frac{0.82}{0.18}$		$\frac{0.90}{0.10}$	$\frac{0.90}{0.10}$	$\frac{0.44}{0.56}$	

[a] D_i is computed from values of N_i in the next column, with $(D/H) = 0.82/0.18$. [b] D_i is computed from values of N_i in the next column, with $(D/H) = 0.90/0.10$. [c] N_i with $(D/H) = 0.90/0.10 + N_2'$ with $(D/H) = 0.44/0.56$. This gives essentially exactly the D_i's observed. [d] M (footnote *d*, Table III) = 2.9, but the accuracy is low because of the low degree of hydrogenation. In run S6 at 13.9% hydrogenation, $M = 2.4$. [e] Observed. [f] (D/H) is the effective value of $(D*/H*)$; *i.e.*, (D/H) is $(D*/H*)$ corrected for kinetic isotope effects, which are assumed to be identical in reactions 3 and 4 of Scheme I.

Table VI. Computation of N_i from D_i

	Run D9 Cyclopentene[a] Solvent THF–D_2SO_4,[c] 3.6°			Run S20 Cyclohexene[b] Solvent THF, 27°		
i	D_i (obsd), %	D_i (calcd), %	N_i, %	D_i (obsd), %	D_i (calcd), %	N_i, %
10	0.1	0.1	0.7	0.0	0.0	0.0
9	0.4	0.3	0.6	0.0	0.0	0.0
8	0.5	0.5	0.6	0.0	0.0	0.0
7	0.7	0.7	1.2	0.05	0.02	0.1
6	1.3	1.4	2.0	0.15	0.1	0.3
5	8.0	8.0	18.3	0.2	0.2	0.4
4	9.7	9.7	4.2	1.0	1.0	2.0
3	15.1	15.1	18.2	6.1	6.1	11.4
2	43.2	44.3	54.2	55.7	56.0	85.8
1	18.6	17.7		31.5	31.9	
0	2.4	2.0		5.3	4.7	
D_{av}	2.50			1.67		
(D/H)[d]			$\frac{0.82}{0.18}$			$\frac{0.77}{0.23}$

[a] 12% hydrogenated, cyclopentene-d_0 = 94.8%. [b] 13% hydrogenated, cyclohexene-d_0 = 91.0%. [c] 1.5 ml of tetrahydrofuran + 0.1 ml of 5% D_2SO_4 in D_2O. [d] See footnote *f* of Table V.

Table VII. Isotopic Distributions of Alkanes from Runs with Various Olefins in Acetic Acid-*d* at about 25°

	1-Hexene	Cyclohexene	Cycloheptene	Cyclooctene	Bicyclooctene	Bicycloctane
Run:	S10	S14	S45	S70	S53	Pt-II[g]
Ane, %[a]	41.2[b]	14.4	14.4	4.1	17.0	
	%D_i					
D_{12}			0.1[c]	0.1[d]		0.4
D_{11}			0.2	0.2		0.6
D_{10}			0.3	0.3	0.0	1.0
D_9	0.0	0.0	0.3	0.3	0.1	1.3
D_8	0.2	0.1	0.6	0.5	2.0	12.9
D_7	0.7	0.2	3.5	0.7	2.6	5.8
D_6	1.4	0.4	5.0	1.1	3.0	4.3
D_5	3.1	0.8	6.2	1.9	5.8	4.2
D_4	7.3	2.5	8.4	4.2	12.2	5.0
D_3	15.5	9.9	13.0	11.0	22.0	6.3
D_2	39.7	61.0	28.0	47.9	34.6	15.5
D_1	23.7	21.2	22.4	25.4	14.3	42.1
D_0	8.4	3.9	12.0	6.3	3.4	(0.0)
D_{av}	2.09	1.92	2.50	2.06	2.80	
Ene-D_0	82.5	91.3	80.1	88.2	84.2	
M[e]	1.4[f]	1.3	2.5	3.6	2.1	

[a] % hydrogenation. [b] Also formed, *trans*-2-hexene, 3.9%; *cis*-2-hexene, 5.4%. [c] % D_{13} = 0.0. [d] % D_{13} = 0.1, % D_{14} + 0.0. [e] Footnote *d* of Table III. [f] Assuming that ene-D_{av} for the 2-hexene was 1.3. [g] Product of isotopic exchange between bicyclo[3.3.0]octane and deuterium on Pt/Al_2O_3 at 68°. D_0 = 80%, D_{13} = 0.4%, D_{14} = 0.3%. The values listed represent the distribution of exchanged material from a run in which 80% of the initial bicyclooctane was unexchanged (from ref 7).

Table VIII. Isotopic Disrtibutions of Alkanes from Runs with Various Olefins in $DOCH_2CH_2ND_2$ Plus CH_3OD[a] at about 25°

	1-Hexene	Cyclohexene[b]	Cycloheptene	Cyclooctene	Bicyclooctene[c]
Run:	S11	S17	S46	S69	S56
Ane, %[d]	38.5[e]	5.5	13.4	6.0	12.0
	% D_i				
D_9					0.0
D_8			0.0	0.0	0.1
D_7			0.1	0.3	0.2
D_6		0.0	0.3	0.7	0.3
D_5	0.0	0.1	0.5	1.4	0.7
D_4	0.8	0.4	1.7	3.9	3.1
D_3	5.3	1.8	6.6	13.4	9.6
D_2	70.1	63.1	65.8	60.8	67.2
D_1	21.7	31.4	22.9	16.9	15.6
D_0	2.1	3.2	2.1	2.6	3.2
D_{av}	1.81	1.65	1.88	2.08	1.99
ene-D_0	89.1	95.2	89.9	77.7	84.7
M[f]	1.0	1.3	1.3	3.2	1.8

[a] Solvent system EA of Table I. [b] 1.45 ml of CH_3OD + 0.05 ml of $DOCH_2CH_2ND_2$. The usual composition gave nearly zero rate of hydrogenation. [c] *cis*-Bicyclo[3.3.0]-2-octene. [d] % hydrogenation. [e] Also formed, *trans*-2-hexene, 1.1%; *cis*-2-hexene, 0.9%. [f] Footnote *d* of Table III.

and ene-D_i's to the true equilibration fractions, ane-N_i's and ene-N_i's. There are, moreover, interesting differences among these solvent systems. The much increased values of (D/H) permit intercomparison between the isotopic composition of alkanes made by hydrogenating olefins with deuterium and the isotopic composition of alkanes made by isotopic exchange between the alkane and deuterium. This intercomparison provides much improved support for the assumption that hydrogenation of alkenes and isotopic exchange of alkanes are closely related mechanistically. Finally, the increased values of (D/H) disclose that the surface of the catalyst is nonuniform and that there are usually at least two different sets of sites on the catalyst surface, one characterized by a large value of (D/H) and the other by a much smaller value.

Exchange between ROD and H* during Hydrogenation. Hydrogenation[13] of neat (Table I) cyclopentene with deuterium on platinum/alumina catalysts gives two products, isotopically exchanged cyclopentene and cyclopentane-d_0 through cyclopentane-d_7 (Table IV). The reactions represent a smearing of the two atoms of deuterium, which adsorb per mole of cyclopentene hydrogenated, among the two positions to which hydrogen adds and the positions which exchange. Since $M = 1.0$, where

$$M = \text{(total moles D in product)}/\text{(twice moles hydrogenated)}$$

there is negligible exchange between H* and D_2(g). The value of M was also 1.0 with the other neat olefins studied. Lack of exchange between H* and D_2(g) was previously observed during reaction between deuterium and 1-hexene on reduced platinum oxide.[5]

During hydrogenation in tetrahydrofuran (THF, Table I), a small amount of exchange between H* and D_2(g) occurs, since $M = 1.3$. The isotopic distributions of cyclopentane are nearly the same in THF and neat, and the fact that the ratio ane-D_2/ane-D_0 is less than unity indicates that (D/H) is less than unity.

Low values of D_{av} (the average number of deuterium atoms in cyclopentane) result from hydrogenating cyclopentene with deuterium in solvents containing hydroxyl groups. With *tert*-butyl alcohol-d_0 as solvent, over 0.75 of the cyclopentane is d_0 (Table II). Thus, exchange between D* and ROH is faster than steps 3 and 4 of the Horiuti–Polanyi mechanism of Scheme I, although probably by less than an order of magnitude. Exchange between H* and ROD proceeds in reaction between *hydrogen* and cyclopentene in *tert*-butyl alcohol-*d* to give a substantial D_{av}, 1.23. Use of *deuterium* and *tert*-butyl alcohol-*d* gives a much increased D_{av}, 2.20. The relatively small value of D_0 shows that the value of (D*/H*) in this run is relatively large. Use of deuterium and *tert*-butyl alcohol-*d* + D_2O gives a still larger value of D_{av}, 2.41, but, as shown by the value of D_0, this is occasioned by more extensive exchange–addition hydrogenation and not by an increase in (D*/H*).

The exchanging solvents of Table IV all show clear breaks following D_5 as do acetic acid-*d* (AcOD, Table V) and ethanolamine-d_3 + methanol-*d* (EA, Table III). Any break in nonexchanging solvents is concealed by the low values of (D*/H*).

Cyclopentene exchanges during hydrogenation mainly to give ene-d_1. Hydrogenation of this gives some ane-d_6 and this causes the break to disappear at higher conversions as shown in Table III for EA. At 1% hydrogenation, $D_5 = 1.6$ and $D_6 = 0.0$. At 9.5% hydrogenation, where ene-D_0 has declined to 81.4, there is still a clear break but D_6 and D_7 have become nonzero. At 29.4% hydrogenation, ene-D_0 = 63.9%, no clear break is identifiable. Thus, formation of exchanged olefin must be kept low if interpretation of the distribution pattern of cycloalkane is not to become confused. Distortion of the pattern at ene-$D_0 > 90\%$ is negligible, but it becomes serious at ene-$D_0 < 80\%$.

As judged by the proportions of D_2, D_1, and D_0, (D*/H*) is about the same in THF–D_2O, THF–D_2SO_4, and AcOD, although it appears to be a little higher in THF–D_2O. AcOD gives much the most exchange–addition hydrogenation, followed by THF–D_2SO_4 and THF–D_2O. In these solvents, ane-D_2 is only about 33% or less. CH_3OD gives about the same ane-D_2 but less exchange–addition hydrogenation and more ane-D_1 and -D_0. Exchange between solvent

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(13) In this paper, the term "hydrogenation" will not specify which isotope of hydrogen is used.

and H* is less efficient in CH_3OD. The solvent system EA behaves differently. It gives less exchange–addition hydrogenation (ane-D_2 is about 67%) and (D*/H*) is substantially larger than in other solvents. The rate of hydrogenation in EA is slow, only about one-tenth that in THF–D_2O. The rates in the other solvents vary little from that in THF–D_2O.

Solvent has some effect upon the ratio

(rate of exchange of olefin)/(rate of hydrogenation)

which is about 0.5 in neat cyclopentene, about 1 in THF, dioxane and CH_3OD, 1.5 in AcOD, 2 in THF-D_2O, and 2.5 in EA. If ene-D_i's were corrected for true exchange, *i.e.*, to concentrations of ene-$(h,d)_i$, the ratios would be increased, and by more than a factor of 2 for the nonexchanging solvents but least of all for EA. That is, the spread in the ratios would be substantially reduced. The values of these ratios are subject to some uncertainty because in most cases we did not establish the absence of poisoning. The necessity for low conversions conflicted with this.

The values of M reflect the rate of exchange between ROD and H* relative to the rate of hydrogenation: THF–D_2O, 2.7; AcOD, 2.4; CH_3OD, 1.7; EA, 2.3; *vs.* THF, 1.3; and neat, 1.0.

Values of N_i and (D/H). The introduction describes a model in which the distribution of ane-D_i's is represented by a set of N_i's associated with one (D/H). However, we have found that one cannot so represent the cyclopentane-D_i's formed in exchanging solvents because one cannot simultaneously accommodate rather large values of D_0 and D_i and substantial values for D_i where i is large.

Cyclopentane-$(d,h)_i$ will appear as ane-d_1, ane-d_{i-1}, ane-d_{i-2}, etc. By the binomial law,[5] the ratio

$$\text{ane-}D_i(i)/\text{ane-}D_{i-1}(i) = (D/H)/i$$

where (i) in the terms at the left refers to contributions from ane-$(d,h)_i$. Whence, when (D/H) is less than 0.83/0.17, N_5 makes a larger contribution to D_4 than to D_5. Thus, for a small enough value of (D/H), fitting D_{i+1}, D_{i+2}, ... may require values of N_{i+1}, N_{i+2}, ... which make contributions to D_i in excess of the observed value of D_i. Giving the most extensive multiple exchange, AcOD exhibits the problem in an extreme form. Consider distribution A of Table V for $(D/H) = 0.82/0.18$. In fitting D_i (obsd), N_7 has really gone negative and N_4 is about to do so. No smaller value of (D/H) can be used, yet large excesses in D_0 and D_1 remain. Distribution B for $(D/H) = 0.90/0.10$ shows a set of N_i's which is more plausible at larger values of i but which gives an even worse fit to D_0 and D_1.

Let us test the assumption that there are two surface pools, (D/H) large and $(D/H)'$ small; a general set of N_i's is associated with (D/H) but only N_2' has a finite value in the primed set. Distribution C shows such a set for $(D/H) = 0.90/0.10$ and $(D/H)' = 0.44/0.56$ which exactly reproduces the observed values of D_i This set is not unique. If $(D/H) = 1.00/0.00$, then $N_3 = D_3$, $N_4 = D_4$, ... The observed values of D_i are now fitted by $N_2 = 18.4\%$ and $N_2' = 31.8$, with $(D/H) = 0.482/0.518$. Similarly, D_i (obsd) can be fitted by $(D/H) = 0.82/0.18$, $N_2 = 27$, and N_3, N_4, ..., N_{10} from distribution A coupled with $(D/H)' = 0.33/0.67$ and $N_2' = 14.4$. These last two distributions represent the extreme limits of possible ones. Distribution C in Table VI for $(D/H) = 0.90/0.10$ is a more plausible possibility.

Despite the lack of uniqueness in particular solutions to the model just described and the fact that more complicated sets of sites could also represent the observed isotopic distributions, it seems clear that our catalyst contains *at least* two different sets of site. On the unprimed sites, (D*/H*) is large, exchange between ROD and H* must be fast, and essentially all of the observed exchange–addition hydrogenation occurs here. On the primed set of sites, (D*/H*)' is small and simple addition hydrogenation predominates. Because of the absence or near absence of exchange–addition hydrogenation, the hydrogen content in (D*/H*)' must come exclusively or predominantly from exchange of olefin. Total exchanged olefin provides more H* than (D*/H*)' requires. Perhaps only a small portion of olefin exchanges at the primed sites and exchange between ROD and H*' is slow. Perhaps, however, a larger fraction of olefin exchanges at the primed sites and exchange between ROD and H*' is appropriately faster. In neat olefin, since desorption of HD is negligible, olefin exchange and olefin hydrogenation occur at the same sites; *i.e.*, the only source of deuterium in olefin exchange is that adsorbed at sites for hydrogenation. In exchanging solvents, this is probably also true but formal proof is lacking.

In some cases the values of the two (D/H)'s may approach one another closely enough to permit a fairly good fit to be obtained on the assumption that there is only one value of (D/H). Thus, in the run with cyclohexene in Table VI, the amount of exchange–addition hydrogenation is small, there are no substantial breaks in the distribution of D_i, and (D/H) is relatively large on the primed sites. A good fit results. In the run with cyclopentene at 3.6° in THF–D_2SO_4, exchange of cyclopentene is very low. D_0 is low and (D/H) large and, therefore, a fairly good fit results. At 24° in the same solvent system (run D8 of Table V), D_0 is substantially larger and a fit with one value of (D/H) cannot be obtained as is generally true of runs in exchanging solvents.

Noncorrelated variations in the isotopic distribution patterns of cyclopentane exchanged with deuterium on a series of palladium catalysts led us to conclude that at least five different types of sites are involved in the reaction.[14] Similar arguments led us to conclude that at least two different sets of sites were involved in the same reaction on supported platinum catalysts.[7] The present work demonstrates the existence of at least two different sets of sites on platinum by a different type of evidence: the existence of at least two different (D*/H*) pools on the surface.

Kemball and Wells[15] have interpreted the isotopic distributions of ethane formed by addition of deuterium to ethylene on palladium[16] in terms of specific values of the relative rate constants and isotope effects for the mechanism of Scheme I. However, their computed values of D_4, D_5, and D_6 are distinctly too small because, we suspect, of heterogeneity in (D/H). The

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

(15) C. Kemball and P. B. Wells, *J. Chem. Soc. A*, 444 (1968).

(16) G. C. Bond, J. J. Philipson, P. B. Wells, and J. M. Winterbottom, *Trans. Faraday Soc.*, **62**, 443 (1966).

distributions cannot be fitted with a single value of (D/H) but they can be exactly fitted by two sets of (D/H) of the type of distribution C in Table V. For example, the ethanes made at −16° and an ethylene pressure of 51 Torr in Table I[16] are exactly fitted by $(D/H) = 0.73/0.27$, $N_6 = 0.9$, $N_5 = 8.0$, $N_4 = 3.0$, $N_3 = 9.2$, $N_2 = 15.5\%$ and $(D/H)' = 0.40/0.60$, N_2; $= 63.4\%$. Since desorption of HD was negligible in these runs, D_{av} for the unprimed sites cannot exceed 2.00. Thus, (D/H) cannot exceed about 0.73/0.27.

Hydrogenation and Exchange of Cyclohexene, Cycloheptene, Cyclooctene, Bicyclooctene, and 1-Hexene. Other olefins resemble cyclopentene in exhibiting exchange–addition hydrogenation and olefin exchange (Tables VII and VIII). Further, the general characteristics of the solvent systems were the same as with cyclopentene.

The relative extent of exchange–addition hydrogenation is the largest with cyclopentene, almost as large with cycloheptene and bicyclooctene, smaller with cyclooctene, and much the least with cyclohexene. 1-Hexene falls between bicyclooctene and cyclooctene.

A marked break follows D_8 in bicyclooctane made in exchanging solvents and D_7 in cycloheptane (Table VII). No break could be detected after D_8 in any run with cyclooctene. However, because of the rather small extent of exchange–addition hydrogenation and the large number of exchangeable hydrogen atoms, D_8 and D_9 were small in cyclooctane and the test for a break was not very sensitive. The small extent of exchange–addition hydrogenation makes any break after D_6 in cyclohexane difficult to observe as shown in Table VII for AcOD. However, a run in AcOD at 5% hydrogenation and one in CH_3OD both gave $D_6 = 0.5\%$ and $D_7 = 0.1\%$. THF–D_2O was similar. Because of the small extent of exchange–addition hydrogenation, EA exhibited breaks only with cyclopentane. 1-Hexene exhibited clear breaks in no solvent system.

The ratio (olefin exchange)/(hydrogenation) varies somewhat from olefin to olefin. Cyclooctene exhibits much the largest ratio and one which varies less from solvent to solvent than that for cyclopentene. Bicyclooctene gives a somewhat smaller ratio than cyclopentene or cycloheptene. Cyclohexene and 1-hexene give the smallest ratios. The ratio ene-D_2/ene-D_1 is larger in bicyclooctene than in other olefins.

Double bond migration cannot be detected by our techniques in simple cycloolefins, nor was isomerization of bicyclo[3.3.0]-2-octene to bicyclo[3.3.0]-1-octene observed. However, isomerization of 1-hexene to 2-hexene appeared in all runs. The ratio *cis*-/*trans*-2-hexene was usually near unity. The ratio isomerization/hydrogenation varied from 0.2 in AcOD to 0.1 neat to 0.05 in EA. In a previous investigation with neat 1-hexene on reduced platinum oxide,[5] the ratio was 0.03 and (olefin exchange)/(hydrogenation) was 0.3 *vs.* 0.5 in the present work. Most of the exchanged hexene is 1-hexene.

The runs with bicyclooctene and cycloheptene in AcOD, THF–D_2O, and CH_3OD provide strong support for our conclusion that at least two sets of sites with different values of (D/H) are involved. In particular, consider the run with bicyclooctene in Table VII. To obtain the observed value of D_8 without making N_7 negative, (D/H) must be greater than 0.86/0.14. Yet this value is too large to give the observed values of D_0 and D_1. The problem is even more acute in the run with cycloheptene because of the relatively larger values of D_0 and D_1.

Mechanism. It has been widely assumed for some years that exchange of alkanes, although much slower, proceeds by the same mechanism as hydrogenation of olefins. Alkane exchange would start by dissociative adsorption (reaction −4 or Scheme I) of alkane. Reactions −4 and 4 alone would give only alkane-d_1, but reactions −4 and 4 coupled with reactions −3 and 3 could lead to alkane with exchange patterns similar to those of olefin hydrogenated with deuterium. However, the small value (D/H) in the latter reaction has made detailed intercomparison difficult in the past.

In exchange of cyclopentane on group VIII metals, D_5 is usually large and D_6 and D_7 are small. D_8–D_{10} vary with metal and with pretreatment of catalyst.[3,5,17] In Table IV, Pt–I shows the isotopic distribution of cyclopentane exchanged on Pt/Al_2O_3.[7] It is characterized by a large maximum at D_5. The interpretation has been that alternation between mono- and diadsorbed cyclopentane, reactions 3 and −3, can exchange all hydrogen atoms on one side of the cyclopentane ring, but the Horiuti–Polanyi mechanism provides no way in which hydrogen atoms on the other side of the ring can exchange.[2,3] Hydrogenations with deuterium in exchanging solvents all exhibit a sharp break after D_5. D_5 is not a maximum, but N_5 probably is a maximum in AcOD and THF–D_2O (Table V). Presumably, there is also a sharp break following N_5 in cyclopentane from hydrogenations in nonexchanging solvents, but there low (D/H) prevents the appearance of a clear break following D_5. Eachange of both sides of the ring in one period of adsorption must proceed by a process additional to the Horiuti–Polanyi mechanism.[3] This occurs both in hydrogenation and exchange on platinum but only to a minor extent (Table IV).

An isotopic distribution for D_1–D_5 like that for Pt–I in Table IV cannot result from a single process with uniform rate constants.[18] Since, in hydrogenation on the primed sites, reaction −3 is slow, it is tempting to ascribe to the primed sites the process which generates the large amount of D_1 in alkane exchange. There are, thus, probably at least three types of sites on platinum, the primed sites (low (D/H) in hydrogenation) and two types of unprimed sites (high D/H), one giving exchange only to cyclopentane-d_5, the other giving exchange beyond d_5. Evidence for the distinction between the latter two comes from exchange studies.[7]

A substantial break following D_7 has been reported for cycloheptane exchanged on evaporated platinum films.[19] The same phenomenon appears in addition of deuterium to cycloheptene in AcOD, THF–D_2O, and CH_3OD. However, exchanged cyclooctane shows no such break, either on platinum[19] or on palladium.[3] No break appears in cyclooctane made by addition of deuterium to cyclooctene. We had interpreted the

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(17) J. R. Anderson and C. Kemball, *Proc. Roy. Soc., Ser. A*, 226, 472 (1954).

(18) J. R. Anderson and C. Kemball, *ibid.*, 223, 361 (1954); H. C. Rowlinson, R. L. Burwell, Jr., and R. H. Tuxworth, *J. Phys. Chem.*, 59, 225 (1955).

(19) B. S. Gudkov, E. P. Savin, and A. A. Balandin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 509 (1968).

exchange result as follows.[3] Cyclopentane can only form cis-eclipsed 1,2-diadsorbed cycloalkane. However, cyclooctane readily assumes a conformation in which trans hydrogen atoms are eclipsed.[20] A trans-diadsorbed cyclooctane transfers the position of adsorption from one side of the ring to the other. Therefore, one expects no break after D_8, since all hydrogen atoms form one set in terms of the Horiuti–Polanyi mechanism. In hydrogenation on platinum, cycloheptene shows little sign of being able to form a trans-eclipsed diadsorbed cycloheptane, but the results indicate that this species forms to some extent on palladium.[3]

Cyclohexane made from cyclohexene and deuterium shows such rapid decline in D_i with increasing i that only a very small break follows D_6. Cyclohexane made by exchange between cyclohexane and deuterium[17] exhibits a clear break following D_6, but the degree of multiple exchange is much less than with cyclopentane. We interpreted similar results on palladium[21] in terms of the difficulty of forming a boat-like conformation of cyclohexane in 1,2-diadsorbed cyclohexane.

Bicyclooctane made by hydrogenation of bicyclooctene with deuterium is particularly interesting. It shows a pattern very like that of bicyclooctane exchanged on Pt/Al_2O_3 (Table VII). In bicyclooctane-d_8, following which a sharp break occurs, all eight deuterium atoms are on one side of the ring and they correspond to positions all of which can be interlinked by alternation between mono- and diadsorbed bicyclooctane.[7]

In sum, then, the isotopic distribution patterns of cycloalkanes made by hydrogenating cycloalkenes are very similar to those made by isotopic exchange between cycloalkane and deuterium. The large value of (D/H) in exchanging solvents has permitted detailed intercomparison of exchange patterns the results of which strongly support the view that alkane exchange and olefin hydrogenation proceed by closely related mechanisms.

The extent of extensive multiple exchange is always smaller in the olefin hydrogenation. However, olefin adsorption is much stronger than alkane adsorption and one would expect a more densely packed surface in olefin hydrogenation. This would impede reaction -3.

Ethanolamine slows hydrogenation considerably and slows exchange–addition hydrogenation more than simple addition hydrogenation. Ethanolamine must adsorb rather strongly and suppress multiple exchange either by increased surface packing or, perhaps, by poisoning the exchange–addition sites. The hydrogenation of cyclohexene is inhibited much more than that of the other olefins and can be effected only in the presence of a much reduced amount of ethanolamine. By operating in our usual EA solvent, one could probably hydrogenate a number of olefins in a mixture without hydrogenating cyclohexene.

As mentioned in the introduction, reactions 2, 3, -3, and -2 of the Horiuti–Polanyi mechanism provide for olefin exchange. However, for many years, there have been suggestions that other mechanisms account for at least part of the isotopic exchange of olefins which occurs on metallic catalysts. Such suggestions have involved, in particular, dissociative adsorption of olefin to vinylic or allylic species.

Smith and Swoap[22] examined the exchange between deuterium and neat cyclohexene on platinum catalysts. Our ene-D_i's on platinum/alumina resemble those which they reported for platinum/carbon and reduced platinum oxide. They also showed by nmr that about equal amounts of deuterium in exchanged cyclohexene were located at vinylic and allylic positions. It being difficult to obtain cyclohexene-d_1 labeled at a vinylic position by the Horiuti–Polanyi mechanism, Smith and Swoap proposed that exchange involved a form of adsorbed cyclohexene-d_1 in which a suprafacial 1,3 shift of a proton occurred.

No matter what the origin of ene-d_1, it would seem simplest to assume that the many-atom exchange of cyclopentene involves the same processes as those which give exchange–addition hydrogenation. However, it is somewhat disconcerting that our distributions for cyclopentene from exchanging solvents do not, in general, show an abrupt decline following ene-D_3. One would expect such a break to parallel that of the break following ane-D_5.

Studies of olefin exchange in exchanging solvents might well be useful as a result of the increased values of (D/H). However, such studies should be coupled with location of deuterium atoms by nmr.

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[20] For a recent discussion, see J. E. Anderson, E. S. Glazer, D. L. Griffith, R. Knorr, and J. D. Roberts, *J. Amer. Chem. Soc.*, 91, 1386 (1969).

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

[22] G. V. Smith and J. R. Swoap, *J. Org. Chem.*, 31, 3904 (1966).