lack of acidic protons with which to form hydrogen bonds.

De Boer and Custers[5] have resolved the spectrum of 4-nitrophenol adsorbed on calcium fluoride into the spectrum due to absorption by the first monolayer of 4-nitrophenol, which is held by electrostatic forces, and the spectrum due to the subsequent layers of the compound, which are held by forces like those in the pure crystalline compound. The absorption attributed by them to the second and following layers corresponds well with our spectrum of 4-nitrophenol in potassium bromide.

Two applications of the present method for measuring spectra are immediately evident. Fieser[29] has suggested that the normally inert carcinogens are activated by adsorption onto genetic material in the cell. A most worthwhile investigation would be that of the spectra of the carcinogens in inert solvents and adsorbed on proteinaceous material and on nucleic acids. Michaelis and Granick[30] already have reported the spectra of histological stains adsorbed on colloidal suspensions of nucleic acid at *p*H 4.6.

Silica gels prepared in the presence of certain compounds and then extensively extracted show increased adsorption affinities for these compounds.[31] Gels prepared in this way retain a small amount of the adsorbate even under vigorous treatment and it would be worthwhile to investigate the firmly held adsorbate spectrophotometrically and compare its spectrum with that of the less firmly held adsorbate.

LOS ANGELES 24, CALIFORNIA

[29] L. Fieser, National Academy of Sciences—National Research Council, Publication 206, Washington, D. C., 1951, pp. 384–385.

[30] L. Michaelis and S. Granick, THIS JOURNAL, **67**, 1212 (1945).

[31] F. H. Dickey, *J. Phys. Chem.*, **59**, 695 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

The Exchange between Hydrocarbons and Deuterium on Palladium Catalysts[1]

BY ROBERT L. BURWELL, JR., BENJAMIN K. C. SHIM AND H. C. ROWLINSON

RECEIVED MARCH 30, 1957

Results of isotopic exchange between deuterium and twelve alkanes and cycloalkanes are reported. Palladium on γ-alumina was principally employed as a catalyst but some work on evaporated palladium and rhodium films is included. At about 150°, the results on both palladium catalysts were similar and also resembled the results with nickel catalysts at this temperature rather closely. At temperatures below 100°, the impregnated palladium catalyst favors more extensive multiple exchange than does nickel. At 110–150°, nearly every molecule of (+)3-methylhexane which is exchanged is also racemized. At 60 to 80°, the initial isotopic exchange patterns of cyclopentane and cyclohexane exhibit marked discontinuities following the species of half-deuteration, cycloheptane exhibits a very small discontinuity and cycloöctane, none. Bicyclo[2.2.1]heptane exchanges only two hydrogen atoms in the initial step. These results are consistent with the assumption that *vic*-diadsorbed alkane (a state presumed to be equivalent to adsorbed olefin) occurs only in the eclipsed conformation.

Recent papers from this Laboratory[2-4] have reported the results of isotopic exchange reactions between deuterium and a number of different saturated hydrocarbons on a variety of nickel catalysts. In the present paper we report the results of a study of isotopic exchange between deuterium and twelve alkanes and cycloalkanes on palladium catalysts. The cycloalkanes: cyclopentane, methylcyclopentane, 1,1-dimethylcyclopentane, cyclohexane, cycloheptane, cycloöctane and bicyclo[2.2.1]heptane have led to results of considerable interest with respect to the mechanism of the exchange reaction and, in particular, of its stereochemistry.

Experimental

Materials.—As the last steps in purification, hydrocarbons were fractionally distilled and percolated through silica gel.

Hexane, 2,3-dimethylbutane and heptane were Phillips Petroleum Co., pure grade. The preparations of 3,3-dimethylpentane and (+)3-methylhexane have been described.[3]

Cyclopentane and methylcyclopentane were Phillips research grades. The former was used as such but the latter contained a trace of impurity absorbing at 15 μ which was removed by percolation through silica gel. 1,1-Dimethylpentane supplied by the American Petroleum Institute, Project 45, and reported to have a purity of 99+% was used as such.

Matheson cyclohexane was purified as described above. Cycloheptane was prepared by Wolff–Kishner reduction[5] of cycloheptanone (Geigy Pharmaceutical Co.), m.p. −8.0°. Cycloöctane was prepared by hydrogenation of cycloöctatetraene (Aldrich Chemical Co.), with platinum oxide in glacial acetic acid at room temperatures and 70 atm.; m.p. 14.3°.

Bicycloheptene[6] was hydrogenated with 70 atm. of hydrogen using nickel–kieselguhr (Harshaw) without solvent to give bicyclo[2.2.1]heptane; m.p. 86–87°. It would be safer to use a solvent to avoid the sudden exothermic hydrogenation which occurs when the autoclave is warmed to the melting point of bicycloheptene.

Purities as estimated by vapor phase chromatography are: cycloheptane, 99.7% or better; cycloöctane, 99.5%; bicycloheptane, 99.5%.

Electrolytic hydrogen was passed through a Deoxo unit (Baker and Co.) and a Dry Ice trap. Deuterium (Stuart Oxygen Company) was similarly purified.

A 3.3% palladium on γ-alumina was prepared by impregnation. A slurry of 26 g. of γ-alumina,[7] in a solution of 5.7 g. of palladium chloride in 100 cc. of water slightly

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[1] Presented at the International Congress on Catalysis, Philadelphia, Pennsylvania, September 9, 1956.

[2] R. L. Burwell, Jr., and W. S. Briggs, THIS JOURNAL, **74**, 5096 (1952).

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

[4] R. L. Burwell, Jr., and R. H. Tuxworth, *ibid.*, **60**, 1043 (1956).

[5] Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

[6] C. L. Thomas, *Ind. Eng. Chem.*, **36**, 310 (1944).

[7] R. P. Eischens and P. W. Selwood, THIS JOURNAL, **69**, 1590 (1947).

acidified with hydrochloric acid was evaporated to dryness on a steam-bath and dried in an oven at 110°. After reduction at 140° in hydrogen for ten hours, no further hydrogen chloride could be detected in the effluent gas stream. The catalyst was cooled in nitrogen, removed from the reduction tube, pelleted, crushed and sieved to 20–40 mesh. Before use, it was treated with hydrogen at 350° for eight hours *in situ*. A similar catalyst containing 13.8% of palladium was used when higher activity was required.

Technique.—Previous flow techniques[3] were employed. The quantity of catalyst, chosen to give desired rates, varied from 0.08 to 18 cc. The mole ratio of deuterium to hydrocarbon in the catalyst feed was about 2 except in experiments with less volatile hydrocarbons at lower temperatures. Here, higher ratios were used. In runs in which the initial isotopic distribution pattern was desired, total conversions were kept low to avoid isotopic dilution of the deuterium with consequent smearing of the distribution pattern. In most such cases, the total number of molecules exchanged was below 3% at which value the hydrogen content of the effluent deuterium was about 6%. Although one might like even less isotopic dilution, accurate analysis is already difficult. The actual percentages of most of the exchanged species are low and subject to error in correction for the background of the mass spectrometer. We believe, however, that our results correctly disclose the essential features of the initial isotopic distribution patterns.

Analysis.—Procedures for mass spectrometry[3] and interpretation of data[2] have been described. In runs in which perdeuterocyclopentane is the predominant species, correction for such species as $C_5D_9^+$, $C_5D_7^+$, are significant. With a few hydrocarbons and particularly bicycloheptane, one must correct for the carbonium ion one unit below the parent peak. The relatively large value of the isotope peak (C^{13}) at one mass unit above the parent peak introduces an error in the % of the monodeutero species of about 0.1 percentage units in the favorable cases. Similarly, the error in the dideutero species is a little larger than with the others.

Experimental Results

Relative rates of exchange of hexane, heptane, cyclopentane, methylcyclopentane and cyclohexane were determined on 3.3% palladium catalyst by bracketing runs of the first four hydrocarbons between runs with cyclohexane by a technique previously described.[3] Results are presented in Table I. In addition, estimates of the relative activities of a number of other hydrocarbons are possible but since these were not bracketed, the uncertainty is much greater. Ones which we believe to be reasonably secure are entered in Table I. Since it is a solid at room temperatures, bicycloheptane had to be fed to the evaporator as a solution in cyclopentane. It is possible to sort out the mass spectrum well enough to make a rough comparison of the relative degrees of exchange of the two compounds. The degree to which bicycloheptane exchanges more rapidly than cyclopentane decreases with temperature.

TABLE I

RELATIVE RATES OF EXCHANGE OF SEVERAL HYDROCARBONS[a]

Hydrocarbon	Relative rates at 110°(Pd)	170°(Pd)	170°(Ni)[b]
Heptane	1.0	1.0	1.0
Hexane	1.0	1.0	
Cyclohexane	3.2	2.7	0.52
Cyclopentane	4.0	3.2	
Methylcyclopentane	5.2	3.7	8.5
2,3-Dimethylbutane	0.5		
3-Methylhexane	1		1.16
3,3-Dimethylpentane	0.5		0.48
1,1-Dimethylcyclopentane	4		
Bicycloheptane		4	
Cycloheptane	10[c]		
Cyclooctane	25[c]		

[a] The first-order rate constants relative to heptane of the formation of molecules of hydrocarbon of all degrees of exchange (see ref. 2 and 3). [b] On reduced nickel oxide at about 170° (ref. 3). [c] Depend upon results at 80°.

Racemization and Exchange of (+)3-Methylhexane.—Table II presents the relative degrees of racemization and exchange of (+)3-methylhexane. The table lists the ratio of the rate constants of the two reactions assuming first-order kinetics[3] and also the fraction of the exchanged molecules which have three or fewer deuterium atoms.

Isotopic Distribution Patterns.—Certain of the isotopic distribution patterns are presented in Figs. 1, 2 and 4 and in Tables III, IV and V. Others relating to the impregnated catalyst are available in the doctoral dissertation of B. K. C. Shim, Northwestern University, 1956.

Discussion

The most interesting and novel conclusions of the present work relate to the stereochemistry of adsorbed hydrocarbon and derive from results of the isotopic exchange of cyclic hydrocarbons. We must present first, however, some generalizations with regard to palladium catalysts and their comparison with nickel ones.

The results of runs with 3-methylhexane and cyclohexane on evaporated palladium films at about 150° resemble those of runs on the impregnated catalysts (see the second and third run in Table III, the first two runs in Table V). Also the run at 50° with cyclopentane (Fig. 1) closely resembles that on evaporated palladium at 25° reported by Anderson and Kemball.[8] Thus, although most of our results were obtained using an impregnated catalyst, we believe that our conclusions apply both to impregnated and to evaporated film catalysts. Evaporated nickel and conventional nickel catalysts are also similar.[3]

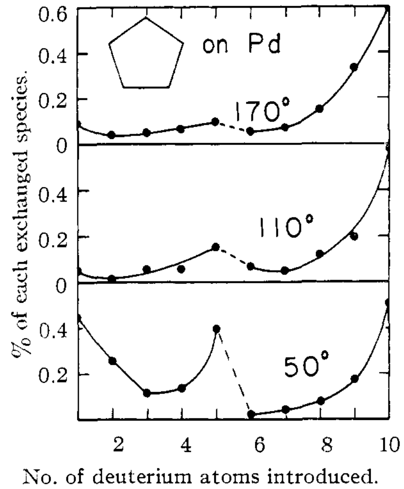

Fig. 1.—Exchange of cyclopentane on palladium-γ-alumina, 13.8% palladium, at 50°, 3.3% at 110 and 170°. D_2/hydrocarbon = 2.

At temperatures in the vicinity of 150°, palladium catalysts and the nickel catalysts of larger

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[8] J. R. Anderson and C. Kemball, *Proc. Roy. Soc.* (*London*), **226A**, 472 (1954).

TABLE II

RACEMIZATION AND EXCHANGE OF (+)3-METHYLHEXANE

Catalyst	13.8% Pd	13.8% Pd	13.8% Pd	13.8% Pd	Evap. Pd	Evap. Pd	Evap. Pd
Temp., °C.	110	110	110	150	150	180	200
Exch., %[a]	22.5	10.0	3.34	26.9	4.8	8.8	13.8
$\Delta\alpha/\alpha_0$, %	18.4	8.5	2.8	24.9	5.6	9.8	13.3
$k_{\text{exch}}/k_{\text{rac}}$[b]	1.3 ± 0.1	1.2 ± 0.1	1.2 ± 0.1	1.1 ± 0.1	0.9 ± 0.2	0.9 ± 0.1	1.0 ± 0.1
Fraction[c] D_1 to D_3	0.26	0.25	0.22	0.20	0.12	0.16	0.16

[a] The % of molecules of alkane which have suffered isotopic exchange. [b] The kinetics are assumed to be first order and k_{exch} represents the rate constant for formation of molecules of all degrees of exchange (see ref. 2). [c] The fraction of the exchanged molecules with 3 or fewer deuterium atoms.

TABLE III

ISOTOPIC EXCHANGE OF CYCLOHEXANE

Catalyst	$Pd-Al_2O_3$[d]	$Pd-Al_2O_3$[e]	Evap. Pd[f]	Evap. Rh	Evap. Rh[g]	Evap. Rh[h]
Temp., °C.	60	170	150	96	100	40
D_2/HC[a]	3.2	2.0	3.0	3.0	3.0	3.0
Flow rate[b]	13.7	18.2	3.8	3.8	3.8	3.8
H_2 in D_2, %[c]	4.5	5.1				
D_0, %	94.7	96.3	93.3	89.7	96.5	86.2
D_1, %	1.5	1.1	1.0	3.0	0.6	3.0
D_2, %	0.47	0.19	0.23	0.73	.11	1.70
D_3, %	.32	.12	.22	.64	.09	1.83
D_4, %	.31	.10	.23	.70	.08	1.92
D_5, %	.28	.12	.24	1.05	.08	2.11
D_6, %	.41	.15	.37	2.17	.11	1.43
D_7, %	.21	.15	.39	0.36	.13	0.49
D_8, %	.25	.16	.43	.26	.16	.45
D_9, %	.28	.21	.52	.26	.36	.32
D_{10}, %	.35	.23	.75	.35	.60	.28
D_{11}, %	.42	.34	1.06	.38	.77	.13
D_{12}, %	.47	.46	1.32	.44	.49	.10

[a] Mole ratio of D_2 to hydrocarbon in reactant stream. [b] Hydrocarbon flow rate in millimoles per hr. [c] Computed % hydrogen in the deuterium at end of catalyst bed. [d] 15 cc. of 13.8%. [e] 0.2 cc. of 3.3%. [f] Wt. of film about 60 mg. but not measured. [g] The Rh film of the previous column was dead after three more runs. It was treated with hydrogen for 18 hr. at 350°. The film weighed 11.8 mg. [h] A new film, 8.2 mg., on its 4th run.

TABLE IV

ISOTOPIC EXCHANGE OF CYCLOHEPTANE AND BICYCLOHEPTANE

	Cycloheptane					Bicycloheptane[e]				
Temp., °C.	60	80	80	80	170	75	155	100	H = 8[f]	H = 12[f]
Cc. cat.[a]	3.0	2.0	2.0	2.3	0.1	2.3	0.08	10		
D_2/HC[b]	6.2	2.0	3.9	4.3	2.1	2.4	2.3	4.3		
Flow rate[c]	10	17	12	12	16	19	20	9		
H_2 in D_2, %[d]	1.0	6.0	2.5	4.7	4.5	2	7			
D_0, %	98.48	98.0	98.2	94.1	98.3	95.8	92.3	11.8	3.6	5.1
D_1, %	0.2	0.02	0.04	1.1	0.07	1.4	3.1	17.0	14.9	17.2
D_2, %	.38	.045	.045	1.13	.045	2.69	4.13	26.7	27.9	26.6
D_3, %	.11	.040	.030	0.48	.040	0.07	0.26	21.4	28.4	25.0
D_4, %	.045	.030	.025	.25	.030	0.04	.11	15.6	17.3	15.6
D_5, %	.030	.035	.030	.15	.030	Nil	.02	5.7	7.3	7.2
D_6, %	.025	.045	.045	.12	.035		Nil	1.6	1.9	2.4
D_7, %	.060	.070	.075	.15	.050			0.3	0.3	0.5
D_8, %	.020	.030	.075	.070	.045			Nil	0.02	.1
D_9, %	.015	.030	.10	.065	.040					.01
D_{10}, %	.020	.050	.13	.075	.065					Nil
D_{11}, %	.020	.075	.20	.095	.11					
D_{12}, %	.030	.15	.25	.21	.17					
D_{13}, %	.085	.42	.33	.61	.21					
D_{14}, %	.48	.95	.45	1.37	.71					

[a] 13.8% Pd. [b] Mole ratio of D_2 to total hydrocarbon. [c] Total hydrocarbon flow rate in millimoles per hr. [d] Computed % hydrogen in deuterium at end of catalyst bed. [e] Fed as solution of 1 vol. bicycloheptane in 2 vol. cyclopentane. [f] Equilibrium distribution ignoring isotope effects for 8 and 12 atoms of hydrogen exchangeable. The total deuterium content in both cases is that of the run on bicycloheptane at 100°.

TABLE V

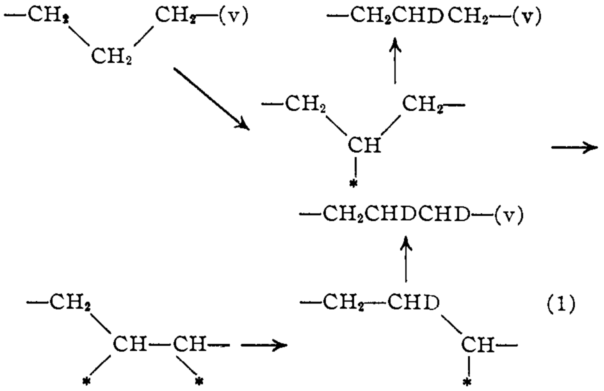
ISOTOPIC EXCHANGE OF CYCLOÖCTANE, (+)3-METHYLHEXANE AND HEXANE

	Methylhexane		Cycloöctane				Hexane
Temp., °C.	110	150	65	80	85	170	110
Cc. cat.[a]	2.0	[b]	3.0	1.0	2.0	0.1	1.0
D_2/HC	2.1	2.0	6.6	7.0	5.7	2.0	2.0
Flow rate	13	3.8	9.5	8.9	11	15	14
H_2 in D_2	7.6		3.1	2.6	10	10	4.2
D_0, %	96.7	95.2	96.6	92.3	90.2	96.9	98.1
D_1, %	0.5	0.3	0.25	1.5	0.6	0.1	0.4
D_2, %	.09	.14	.36	2.51	1.22	.045	.06
D_3, %	.12	.12	.08	1.03	0.37	.030	.050
D_4, %	.10	.14	.055	0.56	.21	.035	.050
D_5, %	.10	.17	.035	.31	.12	.040	.055
D_6, %	.10	.17	.035	.22	.09	.035	.080
D_7, %	.10	.14	.025	.09	.06	.040	.065
D_8, %	.10	.14	.040	.14	.08	.045	.065
D_9, %	.13	.12	.040	.05	.06	.045	.065
D_{10}, %	.14	.14	.040	.10	.08	.055	.075
D_{11}, %	.16	.17	.040	.08	.12	.070	.090
D_{12}, %	.21	.22	.050	.10	.12	.11	.095
D_{13}, %	.30	.31	.050	.10	.16	.20	.20
D_{14}, %	.37	.53	.075	.12	.42	.42	.63
D_{15}, %	.46	.99	.27	.24	1.83	.80	
D_{16}, %	.37	1.15	1.91	.61	4.25	1.04	

[a] 13.8% Pd except in second run, and in run with hexane in which it was 3.3% Pd. [b] Evap. Pd film, estimated weight, 60 mg.

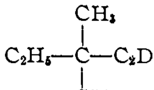
crystallite size[4] give rather similar isotopic distribution patterns as judged by results with hexane, heptane, 3-methylhexane and cyclohexane. At temperatures of 0 to 60°, however, palladium appears to give relatively much more of the multiply exchanged species. Thus, the fraction of exchanged molecules which are extensively exchanged changes much less with temperature with palladium than with nickel. On palladium, the isotopic distribution patterns of hexane, heptane, cycloheptane and cycloöctane change little with temperature.

We believe that the exchange process proceeds basically *via* the following process[9] which combines features of the classical mechanism for the hydrogenation of olefins *via* the half-hydrogenated state.



Where derived from the hydrocarbons we have studied, these intermediates require a more systematic nomenclature than has existed. We shall treat the carbon-surface bonds as substituents in the parent hydrocarbon. Thus, the half-hydrogenated state will be named a monoadsorbed alkane (*e.g.*, 2-monoadsorbed hexane); the adsorbed olefin or two-point adsorption[9] will be called generically *a,b*- or *vic*-diadsorbed alkane and specifically, for example, 2,3-diadsorbed hexane. By extension of this system we have *a,a*- or *gem*-diadsorbed alkane and *a,c*-diadsorbed alkane, neither of which seems important on nickel and palladium catalysts.[3]

Iteration of the alternation between mono- and diadsorbed alkane can lead to any degree of exchange of such molecules as heptane or 3-methylhexane. However, a quaternary carbon atom blocks this propagation reaction and limits exchange to one side chain. Thus, only five hydrogen atoms of 3,3-dimethylpentane, those on one ethyl side-chain, should exchange in one adsorption step to form as the limit


$$C_2H_5-\overset{CH_3}{\underset{CH_3}{C}}-C_2D_5$$

Such limitation is observed on palladium (Fig. 2) as it was on nickel.[2-4] Similarly, exchange cannot propagate from the tetramethylene group of 1,1-dimethylcyclopentane to the methyl groups (Fig. 2).

Eclipsed *vic*-Diadsorbed Alkane.—Since the stereochemistry of *vic*-diadsorbed alkane is not specified, mechanism (1) is incomplete. In the past, the stereochemistry of this state has been largely ignored. Do both C–* bonds lie in the same plane (eclipsed conformation) or does one C–* bond lie between the C–* and a C–H bond on the other carbon atom (staggered conformation) as shown in Fig. 3?

That species which is presumed an intermediate both in exchange of cyclopentane and in hydrogenation of cyclopentene, 1,2-diadsorbed cyclo-

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[9] J. R. Anderson and C. Kemball, *Proc. Roy. Soc.* (*London*), **223A**, 361 (1954).

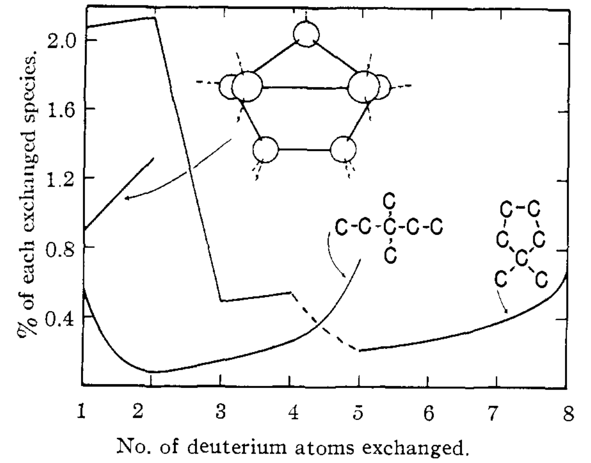

Fig. 2.—Exchange on 13.8% palladium–γ-alumina of bicycloheptane at 118°, of 3,3-dimethylpentane at 110° and of 1,1-dimethylcyclopentane at 60°.

pentane, must be nearly eclipsed since cyclopentane is a nearly planar molecule. The principle of economy of hypothesis suggests that we test the hypothesis that all *vic*-diadsorbed species involve eclipsed conformations. We believe that this hypothesis introduces considerable order into reactions between hydrocarbons and hydrogen (deuterium).

On this view, cyclopentane could exchange at most five hydrogen atoms in one adsorption step since 1,2-diadsorbed cyclopentane could connect only adjacent *cis*-positions. Thus, but one side of the ring could exchange.

Further, 1,2-diadsorbed cyclohexane cannot occur in the rigid (chair) form in which all adjacent bonds are staggered. 1,2-Diadsorbed cyclohexane would necessitate the flexible (boat) conformation in which adjacent, eclipsed bonds exist. Propagation of the exchange reaction could, thus, at most, lead to the exchange of but one of the sets of six *cis*-hydrogen atoms.

In cyclopentane or in cyclohexane, *trans*-hydrogen atoms cannot be eclipsed but in a cycloalkane with many carbon atoms, either *trans*- or *cis*-hydrogen atoms can be eclipsed. Eclipsed *trans*-1,2-diadsorbed cycloalkane would, so to speak, lead from one side of the ring to the other so that all of the hydrogen atoms could exchange rather than but one-half.

In how small a cycloalkane can *trans*-bonds be eclipsed? Models indicate that eclipsed *trans*-1,2-diadsorbed cyclooöctane should form as readily as *cis*. This might even be true with cycloheptane although models suggest that there may be a little strain in attaining a completely eclipsed *trans*-1,2-diadsorbed cycloheptane. A similar stereochemical problem is involved in certain ring fusions.[10]

In fact, cyclooöctane shows negligible discontinuity between $C_8H_8D_8$ and $C_8H_7D_9$ (Table V). The tendency toward perdeuteration is unusually strong and concentrations of species of intermediate degrees of exchange are very low. Cycloheptane exhibits a small discontinuity between $C_7H_7D_7$ and $C_7H_6D_8$ (Table IV). At low temperatures, cyclopentane (Fig. 1) and cyclohexane[8] (see also Table III) exhibit marked discontinuities following half-deuteration as they also do on nickel.[4] These data are in agreement with the hypothesis of eclipsed di-adsorbed alkane although we shall have to explain why perdeuteration occurs at all with these last two hydrocarbons.

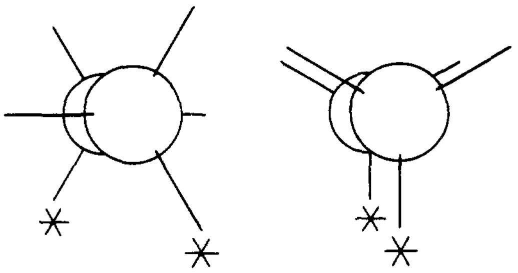

Fig. 3.—Stereochemistry of adsorbed olefin (di-adsorbed alkane).

The results with bicyclo[2.2.1]heptane provide strong support for the assumed stereochemistry. The four pairs of hydrogen atoms on the ethylene bridges (see Fig. 2) are rigidly held in eclipsed conformations. The two hydrogen atoms at the bridgeheads are rigidly held in nearly staggered conformations with respect to adjacent methylene groups. Thus, eclipsed diadsorption is possible on the ethylene bridges but the exchange reaction cannot propagate beyond this position and a maximum of two hydrogen atoms should exchange as is indeed observed (Table IV and Fig. 2) both at high temperatures and at low. A similar effect was observed in this Laboratory by R. H. Tuxworth on a sintered nickel–silica catalyst. From these considerations, one would predict that adamantane would exchange but one hydrogen atom per adsorption step since eclipsed hydrogen atoms are impossible in this molecule.

The geometry of *vic*-diadsorbed alkane must resemble that of a *vic*-disubstituted alkane rather than that of an olefin held by π-bonding.[11] *trans*-Cyclooöctene is a highly strained molecule.[12] Were *trans*-1,2-diadsorbed cyclooöctane to resemble it, the initial products of the exchange of cyclooöctane would contain no species more exchanged than $C_8H_8D_8$.

Racemization.—As shown in Table II, nearly every molecule of (+)3-methylhexane which suffers any exchange is racemized and, considering that some of the exchange involves but a few hydrogen atoms per molecule, it appears probable that nearly every exchange of the hydrogen atom at position-3 leads to racemization at temperatures which have been studied (> 110°).

But mechanism (1) can lead to no racemization.[2] At the time of the original discovery of this same relationship between racemization and exchange on nickel catalysts,[2] we suggested that this mechanism was incorrect. However, the discovery by Anderson and Kemball[8] that cyclopentane and cyclohexane resist exchange beyond half-deuteration made it preferable to retain the basic mechanism and to achieve racemization by a supple-

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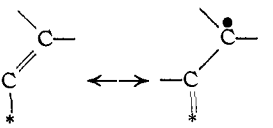
(10) W. Hückel, "Theoretical Principle of Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1955, pp. 106–109.

(11) D. K. Fukushima and T. F. Gallagher, THIS JOURNAL, **77**, 139 (1955).

(12) K. Ziegler and H. Wilms, *Ann.*, **567**, 10 (1950).

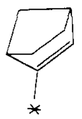
mentary process.[4] Such a process must also permit exchange to propagate from one side of the cyclopentane ring to the other, a reaction which is stereochemically similar to racemization.[4]

Of the several possible intermediates appropriate to this purpose,[2,3,4] an α-monoadsorbed olefin seems preferable.[4]


(2)

As shown in Fig. 1, the relative degree of exchange of cyclopentane beyond half-deuteration increases with temperature and consequently formation of species (2) must be assumed to involve a higher activation energy than any of the steps in the propagation reaction of equation 1. Palladium resembles nickel in this respect.[4]

One may enquire why bicycloheptane does not exchange four hydrogen atoms at higher temperatures. Going to the other side of an ethylene bridge may seem equivalent to going from one side of a cyclopentane ring to the other. If species (2) is the intermediate, one requires 2-monoadsorbed bicycloheptene



Although bicycloheptane is a strained molecule, the introduction of a double bond considerably increases the strain. Thus, exchange of both sides of the ethylene bridge would be much less likely than would perdeuteration of cyclopentane.

Further, at low enough temperatures, (+)3-methylhexane should undergo exchange at the tertiary position without racemization since the frequence of formation of species (2) must be assumed to decline with decreasing temperature. We have not observed this on palladium but we could not study exchange below 110° because of the relative slowness of reaction of 3-methylhexane (Table I) and the necessity for rather extensive degrees of conversion in the racemization studies. However, in preliminary experiments on evaporated rhodium films we obtained a run at 100° in which 3-methylhexane was 81% exchanged but only 41% racemized. Thus, $k_{\mathrm{exch}}/k_{\mathrm{rac}}$ is 3.1. At least in exchange reactions, rhodium does not readily form species (2) or whatever species is responsible for racemization and perdeuteration. This also appears in exchange of cyclohexane (Table III, runs 4 and 6). The degree to which the racemization reaction occurs may be influenced by the previous history of the catalyst. Thus, an evaporated rhodium film which had become dead upon use, probably by poisoning, was partially revivified by treatment with hydrogen at 350°. Although little cyclohexane had exchanged beyond $C_6H_6D_6$ on the fresh film, most exchanged beyond $C_6H_6D_6$ on the revivified one (Table III, runs 4 and 5).

One can now interpret the rather complicated isotopic exchange pattern exhibited by methylcyclopentane at 50° in which discontinuities follow $C_6H_8D_4$ and $C_6H_4D_8$ as shown in the full (upper) line of Fig. 4. The four hydrogen atoms *cis* to the methyl group (solid bonds on the formula in Fig. 4) can exchange *via* alternation between mono- and di-adsorbed cycloalkane as in 1,1-dimethylcyclopentane (Fig. 2). However, exchange cannot propagate to any of the other hydrogen atoms *via* eclipsed diadsorbed cycloalkane alone. The five hydrogen atoms on the other side of the ring (dashed bonds) can exchange as a set and eclipsed 1,α-diadsorbed methylcyclopentane can connect these with the methyl hydrogen atoms as shown in the diagram of Fig. 4. Thus, these constitute a set of eight exchangeable hydrogen atoms.

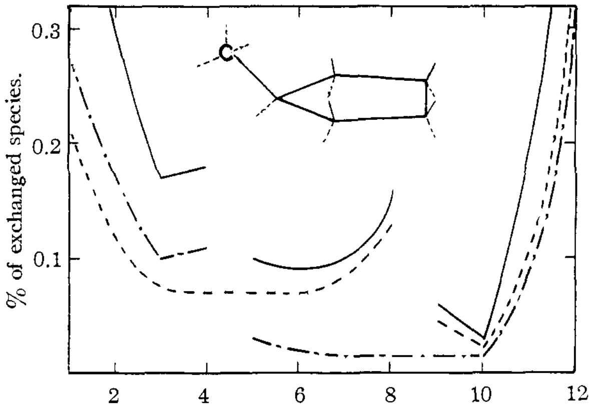


Fig. 4.—Exchange of methylcyclopentane at 50° on 15 cc. of 13.8% palladium-γ-alumina; $D_2/HC = 3$; hydrocarbon flow rate = 13 m*M* per hr.; 2.8% H_2 in exit deuterium. $D_1 = 0.5$, $D_{12} = 0.72$.

If initial monoadsorption involves the 4-set, a discontinuity should follow $C_6H_8D_4$ in runs at 50° as shown by — - — - in Fig. 4. Formation of monoadsorbed methylcyclopentene leads to the second portion of this curve. Similarly if initial adsorption involves the 8-set, - - - - results and the discontinuity follows $C_6H_4D_8$. The sum of two such processes would give the observed curve. As with cyclopentane, the discontinuities were not observed at 170° but were observed in runs at 40, 50, 60 and 80°. Some deviations in detail were observed in runs with different batches of catalyst but the discontinuities always were present.

Reproducibility.—The runs with cycloheptane at 80° in Table IV show deviations in an extreme form. The first two were on the same catalyst and were separated only by a run with 3-methylhexane at 150°. The third run was nearly a duplicate of the second but on a different loading of catalyst. Considerable differences between the second and third runs are apparent in the amount of mono- and dideuteration compared with perdeuteration and also in the discontinuity following half-deuteration.

At the temperatures of most of our runs, bulk palladium would form the hydrogen-rich phase,[13]

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[13] A. Sieverts and W. Danz, *Z. physik. Chem.*, **B34**, 158 (1936); A. A. Alchudzhan and A. V. Frost, *Zhur. Fiz. Khim.*, **26**, 1007, 1015 (1952); *C. A.*, **47**, 956 (1953).

but we have no information as to the exact states of our palladium catalysts. Variations in hydrogen *absorption* may be responsible for some of the variations in exchange patterns. On the whole, however, variations in exchange patterns were minor.

Relative Rates of Exchange.—The rate of production of exchanged hydrocarbon molecules of all degrees of exchange is equal to the rate of adsorption of hydrocarbon. The relative rates of exchange listed in Table I provide some information as to the nature of the transition state in this process.

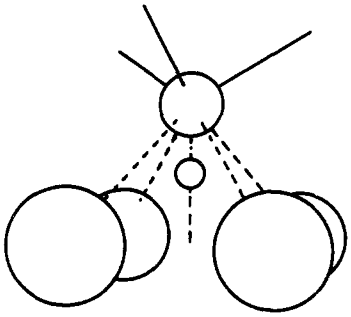

Fig. 5.—Possible transition state separating alkane (v) and monoadsorbed alkane.

In part, high reactivity seems to be correlated with low bond dissociation energies.[14] Hydrocarbons with only primary hydrogen atoms react slowly: methane and ethane,[15] neopentane.[3,16] Secondary hydrogen atoms in propane exchange more rapidly than the primary ones.[17] The tertiary hydrogen atom in isobutane exchanges rapidly.[17]

The sequence cycloheptane > cyclopentane > cyclohexane suggests that the transition state provides some relief from the strain occasioned by eclipsed hydrogen atoms.[18] Bonding of monoadsorbed alkane by multiple partial bonds as in interstitial carbides could account for this. A possible transition state is shown in Fig. 5 in which the separated hydrogen atom initially proceeds to below the surface.[19] Alternatively the hydrogen atom might move sidewise with a geometry somewhat resembling that of an SNi reaction.

The larger number of partial bonds in the eclipsed than in the staggered *vic*-diadsorbed alkane would stabilize the eclipsed conformation.

We have postponed until this place a possible objection to an eclipsed *vic*-diadsorbed species. 2,3-Dimethylbutane exhibits an isotopic exchange pattern little different from that of hexane or 3-methylhexane. For exchange beyond seven hydrogen atoms in one adsorption step with 2,3-dimethylbutane, one requires 2,3-diadsorbed-2,3-dimethylbutane which involves two sets of eclipsed methyl groups. Perhaps, however, the enthalpy of adsorption at two tertiary positions compensates for the additional eclipsing strain.

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[14] A. F. Trotman-Dickenson, "Gas Kinetics," Butterworth Scientific Publications, London, 1955, p. 15.

[15] K. Morikawa, N. R. Trenner and H. S. Taylor, This Journal, **59**, 1103 (1937).

[16] C. Kemball, *Trans. Faraday Soc.*, **50**, 1344 (1954).

[17] C. Kemball, *Proc. Roy. Soc.* (*London*), **223A**, 377 (1954).

[18] H. C. Brown, R. S. Fletcher and R. B. Johannesen, This Journal, **73**, 212 (1951).

[19] A similar proposal has been made for hydrogen chemisorption, M. E. Winfield, *Rev. Pure Appl. Chem.*, **5**, 217 (1955).

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Photochemical Technique

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The range of concentration and wave length over which a photochemical reaction can be studied usefully may be increased if a mirror is used to reflect transmitted light back into the reaction system. This makes the intensity distribution much more uniform and so allows a reaction not directly proportional to intensity to be studied at higher concentration than would otherwise be possible. The necessary theory and an experimental method for determining the reflectivity of the mirror is given.

1. Introduction

The range of concentration, or of wave length, over which a photochemical reaction can be studied is often quite severely limited by the optical properties of the light-absorbing species. At one limit absorption may be strong enough to cause a very non-uniform distribution of intensity, a most undesirable feature when the reaction rate is not directly proportional to intensity. At the other limit absorption may be so weak that it is difficult to obtain satisfactory rates with convenient intensities, or it may be necessary to decompose a significant proportion of the reactants if products are to be obtained in measurable quantities.

The main object of this paper is to show how the useful range of study may be extended by using a mirror to reflect transmitted light back into the reaction medium. This gives a gain of intensity at low absorptions, but also has the more important effect of greatly increasing the uniformity when the

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