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THE INTERACTION OF DEUTERIUM AND SATURATED HYDROCARBONS ON
NICKEL CATALYSTS

By H. C. Rowlinson, Robert L. Burwell, Jr. and Richard H. Tuxworth

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Abstract

The interaction of deuterium and a variety of alkanes and cycloalkanes on evaporated nickel films and on a reduced nickel oxide catalyst leads to very similar results. Isotopic exchange occurs conveniently at 150-200° to produce species with from one to all hydrogen atoms exchanged. With hexane and 3-methylhexane, the most abundant species are those of extensive but not total exchange. With cyclopentanes cyclohexanes and 2,3-dimethylbutane, the most abundant is the fully exchanged one. In cycloalkanes no anomaly appears in the concentration of the species in which one-half of the hydrogen atoms are exchanged. Under the experimental conditions hydrogenolysis of carbon-carbon bonds occurs only with ethylcyclobutane, in which case its rate is comparable to that of exchange.

The data seems to require initial adsorption of the hydrocarbon molecule with cleavage of a carbon-hydrogen bond. The point of attachment then shifts in an α - β process with isotopic exchange accompanying each shift. α - α and α - γ shifts are relatively uncommon. A single branch in the carbon skeleton does not impede migration of the point of attachment but a gem-dimethyl group blocks it. Since racemization of (+)3-methylhexane is closely correlated with the total number of molecules exchanged, a symmetric intermediate is required during the exchange process.

A recent paper from this laboratory³ presented a study

(2) R. L. Burwell, Jr., and W. S. Briggs, J. Am. Chem. Soc.,
74, 5096 (1952).

of the interaction of hydrogen and deuterium with heptane, (+)3-methylhexane, 3,3-dimethylhexane and 2,2,3-trimethylbutane on a nickel-kieselguhr catalyst. Of those molecules which exchanged, most suffered exchange of many hydrogen atoms. Most of the molecules of (+)3-methylhexane which were exchanged were also racemized. It appeared that initial adsorption of alkane involves dissociative adsorption with rupture of a carbon-hydrogen bond followed by migration of the point of attachment of the alkyl fragment with consequent isotopic exchange. With (+)3-methylhexane, at some stage a symmetric intermediate is formed. It seemed wise to see in how far these initially rather surprising results are characteristic of nickel catalysts in general. This paper reports a study of eleven alkanes and cycloalkanes on evaporated nickel films, on reduced nickel oxide and on another type of nickel-kieselguhr catalyst.

Experimental

Materials.- The following Phillips Petroleum Company Research Grade hydrocarbons were used without treatment: cyclopentane, methylcyclopentane and methylcyclohexane. Heptane was percolated through silica gel and fractionated in a 50-plate Podbielniak Heli-Grid column, n_D^{25} 1.3853. Phillips Pure Grade 2,3-dimethylbutane was similarly treated, n_D^{25} 1.3724, as was Eastman Kodak Company cyclohexane, n_D^{25} 1.4234. Neopentane was kindly furnished by Professor H. Pines and 1,1-dimethylcyclohexane, 99.9 mole % pure, by Dr. Kenneth Greenlee of the American Petroleum Institute Project 45,

Dr. Cecil Board, director, at the Ohio State University.

3,3-Dimethylpentane was prepared by interaction of t-amyl chloride and ethylene in the presence of aluminum chloride at -40° .³

(3) L. Schmerling, ibid., 67, 1152 (1945).

The resulting 1-chloro-3,3-dimethylpentane was converted to 3,3-dimethylpentane by preparing and hydrolyzing the Grignard reagent. After preliminary distillation, the material was percolated through silica gel and distilled in the 50-plate column, n^{25}_D 1.3886.

Ethylcyclobutane was prepared by R. G. Armstrong following Pines, Huntsman and Ipatieff,⁴ n^{20}_D 1.4018. It was percolated and

(4) H. Pines, W. D. Huntsman and V. N. Ipatieff, ibid., 75, 2315 (1953).

distilled as above.

(+)3-Methylhexane was prepared from active amyl bromide⁵ by

(5) R. L. Burwell, Jr., and G. S. Gordon, III, ibid., 70, 3128 (1948).

reaction of the Grignard reagent of this compound with acetic anhydride at -78° .⁶ The resulting 4-methyl-2-hexanone was reduced to the hydro-

(6) M. S. Newman and A. S. Smith, J. Org. Chem., 13, 592 (1948).

carbon by the Wolff-Kishner method.⁷ The product was distilled,

(7) Huang-Minlon, J. Am. Chem. Soc., 68, 2487 (1946).

percolated through silica gel and distilled on the 50-plate column.

The infra-red spectra of several batches were shown identical with those of the Bureau of Standards Standard Sample of this hydrocarbon by a substitution method. This method of preparation is superior to

the one formerly described.²

Tank deuterium gas was secured from the Stewart Oxygen Company under allocation from the Atomic Energy Commission. Before use it was passed over copper at 450° and then through a Dry Ice trap.

The nickel catalyst was prepared by Mr. W. S. Briggs from nickel carbonate which was precipitated from a solution of nickel nitrate by the rapid addition of sodium carbonate. The precipitate was thoroughly washed by decantation, filtered, dried at 110° and treated with oxygen at 300° for four hours. 20-40 mesh material was selected and reduced at 300° in hydrogen before placing in the catalyst chamber where it was rereduced. Harshaw Chemical Company's nickel-kieselguhr catalyst was crushed and 20-40 mesh material was selected.

Analysis.- Products were examined on the Baird recording infrared spectrograph. The C-D band at 4.6 microns was used to get an immediate estimate of the degree of exchange and to select suitable samples for mass spectrographic analysis.

Mass spectrographic analyses of hydrocarbons of molecular weight of 98 and higher were performed on a Consolidated mass-spectrometer under the direction of D. V. Kniebes at the Institute of Gas Technology, Chicago, Illinois. Those of lower molecular weight were examined on a manual Westinghouse mass-spectrometer in the Department of Chemical Engineering at Northwestern University under the supervision of D. M. Mason. Relatively high pressures of hydrocarbon were used to get as much sensitivity in the determination of the isotopically exchanged species as possible. The % of each exchanged species was computed from the parent peaks save for neopentane in which case mass 57 was employed and 3,3-dimethylpentane, mass 85. The treatment of the mass spectroscopic data was as before.²

Precision in the % of the various exchanged species is about 0.03 percentage units or about 5% of the listed figure for the more heavily exchanged samples. The % of D_1 is less accurate since the unexchanged species containing one atom of C^{13} has the same mass and correction must be made for this. The probable error in the fraction of molecules exchanged is about 10%.²

Evaporated nickel films.- Evaporated nickel films were prepared by customary procedures including careful degassing at elevated temperatures. Owing to the necessity of collecting enough 3-methylhexane for polarimetry, the scale of operation was much larger than that generally used by previous workers.

The catalyst chamber was a section of glass tubing 45 mm. in inside diameter and between 50 and 75 mg. of nickel was evaporated onto the inner surface of this tube while the tube was cooled in ice-water. Gaseous mixtures of deuterium and hydrocarbon were prepared by bubbling deuterium gas through a sample of previously degassed hydrocarbon held at a suitable temperature. The mole ratio of deuterium to hydrocarbon was about 3 save with (+)3-methylhexane in which it was about 2. The reactant stream entered at the bottom of this tube via 8 mm. tubing coiled helically around the large tube so that the reactant stream would be at reaction temperatures before entering the catalyst chamber. A furnace surrounded the catalyst tube. A hemispherical shell of glass about 40 mm. in diameter was placed open end up immediately above the joint of the entrance tube to the catalyst tube. This served to start the gas stream up the inner face of the catalyst tube.

The effluent stream was passed into a trap cooled with liquid nitrogen and containing a calibrated section of small bore tubing at the bottom. Flow rates lay between 0.3 and 0.7 cc. of liquid hydro-

carbon per hour.

Nickel catalysts.- Experiments on reduced nickel oxide and on nickel-kieselguhr were run in an apparatus which will be described elsewhere. It is generally similar to that formerly used² but contains a positive action pump delivering degassed hydrocarbon into an evaporator provided with deuterium flow. 2 cc. of catalyst was employed. Flow rates were about 3.4 cc. of liquid hydrocarbon per hr. and of deuterium, 0.0265 moles per hour. The catalysts were reduced initially at 325°. The catalyst from nickel oxide declined in activity with use. Activity could be restored by repeating the treatment with hydrogen at 325°.

Experimental Results

Results of experiments on evaporated nickel films are shown in Table I. Exchange occurred at convenient rates between 130 and 200°.

From the data of Beeck, Smith and Wheeler³ one expects evaporated

(8) O. B. Beeck, A. E. Smith and A. Wheeler, Proc. Roy. Soc. (London),
A177, 63 (1940).

nickel films to have surface areas of 10 sq. meters per gram at 0°. About 0.22 cc. of vapor (STP) would, then, completely cover the surfaces of our films in adsorption with two point attachment. This would apply to films at 0°, sintering would reduce this figure. It is not surprising that we had some troubles with poisoning. After a run, the hydrocarbon in the evaporator was often replaced by another. Attempt was made to avoid the introduction of oxygen during this process. It was commonly possible to get two runs on the same film and occasionally three before serious loss of activity occurred. Particularly in early runs, there seemed to be some variation in initial

TABLE I

INTERACTION OF HYDROCARBONS AND DEUTERIUM ON NICKEL FILMS

Run no. ^a	5a	5b	5c	10a	10b	12a	13a ^d	13b	15a	16b	18a
Hydrocarbon ^b	S	S	S	S	S	33MP	S	23ME	neop	CP	CH
Temp. °	100	130	200	170	130	200	200	200	200	200	200
% Exchange ^c	nil	2.1	18.7	15.0	6.9	12.4	58.8	4.4	1.6	9.7	14.0
% D ₁	0.16	0.86	0.77	0.37	2.60	1.95	5.88	0.62	1.38	0.98	2.95
D ₂	.12	.54	.70	.31	1.22	0.83	5.66	0.23	.12	.59	0.33
D ₃	.12	.53	.65	.33	3.70	.71	5.36	0.20	.08	.53	.13
D ₄	.11	.69	.51	.24	2.77	.41	3.14	0.15	nil	.50	.11
D ₅	.11	1.04	.45	.21	2.00	.71	1.47	0.20	.11	.57	.15
D ₆	.11	1.53	.43	.20	.18 ^k	1.12	.45 ^k	0.15	.71	.71	.21
D ₇	.12	2.11	.52	.24	nil	1.81	0.15	0.15	1.04	1.04	.34
D ₈	.12	2.48	.55	.26	.26	3.15	0.18	0.18	1.78	1.78	.60
D ₉	.14	2.49	.66	.31	.31	5.16	0.20	0.20	1.91	1.91	1.14
D ₁₀	.14	2.18	.94	.44	.44	6.76	0.20	0.20	1.87	1.87	2.01
D ₁₁	.19	1.66	1.26	.59	.59	7.96	0.26	0.26	2.95	2.95	2.95
D ₁₂	.19	1.18	1.64	.77	.77	8.24	0.41	0.41	3.19	3.19	3.19
D ₁₃	.20	0.78	1.85	.87	.87	7.37	0.48	0.48			
D ₁₄	.14	.49	1.68	.79	.79	5.90	1.00	1.00			
D ₁₅	.09	.25	1.40	.59	.59	4.24					
D ₁₆	.05	.07	0.92	.39	.39	2.51					

19a ^p	19b ^f	21a	23b ^g	22a ^{h,i}	22b ^j	22c
3MH	3MH	11MCH	ECB	3MH	3MH	CP
200	130	301	150	200	150	150
34.7	4.9	5.2	?	50.3	11.6	4.2
2.08	0.44	1.49	3.03	1.56	0.62	0.59
1.05	0.29	0.29	1.63	1.09	.40	.57
0.93	0.22	.18	1.07	1.12	.40	.36
1.05	0.28	.12	0.90	1.72	.63	.32
1.27	0.30	.15	1.01	2.68	.94	.24
1.59	0.30	.20	1.29	3.97	1.16	.24
2.69	0.47	.21	1.74	5.39	1.50	.27
3.51	0.56	.47	2.03	6.04	1.50	.36
4.00	0.62	.86	2.41	5.98	1.40	.51
4.00	0.56	1.21	2.48	5.28	1.10	.80
3.52	0.45	.07 ^k	2.26	4.36	0.78	
2.88	0.30	nil	1.74	3.47	.59	
2.12	0.15		1.18	2.70	.21	
1.49			0.68	2.15	.19	
1.35			.28	1.69	.13	
1.01			.23	1.18	.03	

Notes for TABLE I

^aThose runs with the same number were run on the same film in the order indicated by the letter. ^bS is heptane; 33MP, 3,3-dimethylpentane; 23MB, 2,3-dimethylbutane; neoP, neopentane; cP, cyclopentane; cH, cyclohexane; 3MH, 3-methylhexane; 11McH, 1,1-dimethylcyclohexane; and EcB, ethylcyclobutane. ^c% of total hydrocarbon molecules which have suffered exchange. ^dDeuterium was bubbled through a mixture of heptane and 3,3-dimethylpentane. The exchange of the two hydrocarbons could be separately analysed. ^e32.0 % loss in optical rotation. ^f3.4 % loss in rotation. ^gHydrogenolysis accompanied this run. The sum of the peaks at masses 84-100 was set at 100% and the height of each mass peak above 84 entered as %. ^hRuns 22a, 22b and 22c were on an oriented film prepared by evaporating nickel in 1 mm. of nitrogen. The weight of the film was but 12.4 mg. ⁱ47.4% loss in rotation. ^j9.5% loss in rotation. ^kThese values can be substantially accounted for by a second adsorption of a molecule already once exchanged.

TABLE II

INTERACTION OF HYDROCARBONS AND DEUTERIUM ON REDUCED

NICKEL CATALYSTS

Run No.	B17 ^b	B23 ^c	B115 ^b	B105 ^e	107 ^e	122	124	136	137	140	141	144	150	151	153
Hydrocarbon ^a	3MH ^d	3MH ^e	S	S	2MH ^f	3MH ^g	S	3MH ^h	S	S	33MP	cH	S	MCP	3MH ⁱ
Temp. ^o	128	100	86	96	114	160	156	176	176	210	210	176	160	160	210
% Exchange	6.72	8.51	6.08	5.8	12.7	4.1	3.0	7.8	6.4	15.2	7.7	2.6	2.2	15.9	15.0
% D ₁	1.61	1.15	0.95	0.50	1.45	0.33	0.13	0.79	0.32	0.60	2.31	1.14	0.05	1.3	1.25
D ₂	0.99	0.86	1.10	.45	0.73	.24	.15	.43	.28	.45	1.07	.05	.11	1.6	0.64
D ₃	.92	.83	0.70	.45	.85	.23	.13	.45	.20	.51	1.82	.04	.10	0.9	.53
D ₄	.78	.65	.47	.35	.73	.17	.09	.53	.19	.75	1.27	.03	.11	.8	.64
D ₅	.68	.55	.39	.25	.73	.17	.09	.45	.16	1.11	0.80	.03	.09	.9	.82
D ₆	.47	.47	.33	.25	.65	.17	.08	.20	.11	1.55	.12	.03	.07	1.0	1.05
D ₇	.34	.42	.27	.25	.73	.17	.09	.28	.13	1.99	.06	.05	.07	1.6	1.52
D ₈	.22	.40	.23	.25	.73	.17	.08	.26	.16	2.18	.05	.05	.06	2.0	1.90
D ₉	.17	.37	.22	.25	.85	.19	.08	.39	.24	2.08	.03	.09	.06	2.1	2.08
D ₁₀	.15	.40	.22	.35	.85	.17	.05	.39	.39	1.65	.05	.21	.05	1.9	1.78
D ₁₁	.14	.42	.22	.35	.97	.17	.08	.56	.66	1.13	.04	.42	.05	1.2	1.34
D ₁₂	.10	.46	.22	.45	.97	.23	.13	.84	.94	.66	.03	.52	.07	.6	.82
D ₁₃	.09	.48	.22	.45	.97	.33	.24	.81	1.05	.31	.03	.13	.13	.41	.41
D ₁₄	.06	.47	.19	.45	.65	.46	.48	.70	.88	.12	nil	.27	.27	.17	.17
D ₁₅	nil	.40	.19	.45	.52	.52	.65	.53	.53	.06	.46	.46	.46	.09	.09
D ₁₆	.18	.16	.16	.35	.40	.40	.46	.17	.17	.02	.41	.41	.41	nil	nil

Notes for TABLE II

^a3MH is 3-methylhexane; S, heptane; 33MP, 3,3-dimethylpentane; cH, cyclohexane; McP, methylcyclopentane. ^bFrom Table IV, ref. 2. On UOP nickel-kieselguhr. ^cOn Harshaw nickel-kieselguhr. ^dLoss in optical rotation, 2.1%. ^eLoss in rotation, 6.1%. ^fLoss in rotation, 7.7%. ^gLoss in rotation, 2.9%. ^hLoss in rotation, 4.9%. ⁱLoss in rotation, 13.0%.

activity of the different films.

Methylcyclopentane (run 13c) and methylcyclohexane (run 20a) gave exchange patterns on evaporated nickel films which resembled cyclopentane (run 16b) and cyclohexane (run 18a) closely save that two more exchangeable hydrogen atoms appeared in each case.

Runs of heptane and (+)3-methylhexane on nickel-kieselguhr catalysts and of these hydrocarbons and 3,3-dimethylpentane, cyclohexane and methylcyclopentane on reduced nickel oxide are presented in Table 2.

The relative rates of exchange of these five hydrocarbons were determined on the reduced nickel catalyst in order to compare them with the relative rates of exchange of several hydrocarbons published previously.² Runs on the other hydrocarbons were sandwiched between two runs on heptane. The catalyst was assumed to be in the same state throughout if the depth of the C-D absorption band in the heptanes was nearly the same. One of the heptanes was examined mass spectroscopically. The percentage of heptane molecules exchanged thus found was corrected to the average value for the two reference runs on the basis of the absorption at the C-D band (4.6 microns). In one case, runs 35 and 37, the heptane runs differed by 10%, in the other cases by no more than 3%. Duplicate agreeing sets of runs are available for 3,3-dimethylpentane and methylcyclopentane.

Where the mass spectroscopic patterns permit unequivocal sorting of the exchange patterns of two different hydrocarbons, a mixture of hydrocarbons may be passed over a catalyst and the relative rates thus determined. An example of this is shown for run 13a, Table I for heptane and 3,3-dimethylpentane. Since the latter compound has a negligible parent peak, there is no interference with the heptane

analysis. 3,3-Dimethylpentane has a large peak at mass 85 and heptane has a small peak the effect of which can be subtracted out.

Data on relative rates of exchange are presented in Table III in terms of the number of molecules of hydrocarbon exchanged referred to heptane as 1.0. It was assumed that the rate of appearance of exchanged molecules was first order in unexchanged molecules. Thus the relative rate is

$$\ln \underline{Z} / \ln \underline{Z}_0$$

where \underline{Z} is the fraction of molecules which has not exchanged and \underline{Z}_0 that fraction for heptane under the same conditions. Since cyclohexane and methylcyclopentane, were fed at the same liquid volume rate as heptane, correction was made for contact time.

On nickel catalysts, the rate of exchange of 3-methylhexane is about the same as heptane, that of molecules containing gem-dimethyl groups and short side chains is smaller: 3,3-dimethylpentane, 3,3-dimethylhexane, 2,2,3-trimethylbutane. Neopentane, (Table I, run 15) exchanges very slowly. Cyclohexane exchanges more slowly than heptane but its isomer, methylcyclopentane, exchanges much more rapidly.

The nickel films were derived from 0.020 in. nickel wire manufactured by the Drive-Harris Company. Emission spectroscopy indicated the presence of copper, 0.02%; iron, 0.03%; magnesium, 0.4%; manganese, 0.3% and silicon, 0.02%. Since but 15-20% of the wire was evaporated, one cannot say just what the analysis of the film would have been. Presumably, particularly volatile impurities would concentrate in the first part of the film. In one experiment, about 40 mg. of nickel was evaporated. This film was removed and a film made from the remaining wire. This film corresponded in activity to

TABLE III

Rates of Exchange Relative to Heptane^a

	Evaporated nickel films	UOP nickel- kieselguhr ^b	Reduced nickel oxide
Heptane	1.0	1.0	1.0
3-Methylhexane		0.75 (120°)	1.16 (176°)
3,3-Dimethylpentane	0.27 (200°)		0.48 (210°)
3,3-Dimethylhexane		0.36 (86°)	
Cyclohexane			0.52 (176°)
Methylcyclopentane			8.5 (160°)
2,2,3-trimethylbutane		.13 (120°)	

^aThe relative rates are followed by the temperature at which the comparison with heptane was made. ^bFrom ref. 2.

runs 10, 15 and 19. The exchange patterns of 3-methylhexane and cyclohexane were indistinguishable from those obtained in the usual manner.

Discussion

In general, hydrocarbons undergo extensive exchange with deuterium in the presence of evaporated nickel films, reduced nickel oxide and Harshaw nickel-kieselguhr. The exchange patterns resemble those previously found on another nickel-kieselguhr² but there was relatively less of the more extensively exchanged species with that catalyst.

As previously proposed,² the exchange reaction seems to require initial adsorption of the alkane with cleavage of a carbon-hydrogen bond followed by migration of the position of attachment with consequent exchange of one deuterium atom for each such migration.

The propagation reaction (that is, the migration of the position of attachment) is not significantly affected by the presence of a single branch in the alkane. This is most clearly shown by comparison of heptane with 3-methylhexane, for example, Table II, runs 22 and 24. Nor do two branches on different carbon atoms interfere as is shown by the exchange pattern of 2,3-dimethylbutane, Table I, run 13b.

However, as previously found for 3,3-dimethylhexane,² a double branch on the same carbon atom blocks the propagation reaction. This is further shown by 3,3-dimethylpentane in which only one of the ethyl groups exchanges (Table I, run 12a; Table II, run 141). The slight concentration of species containing more than five deuterons results from double adsorption of the same molecule, the probability of which is $1/2x^2$ where x is the fraction of molecules which have exchange once.²

Similar limitation of the exchange of 1,1-dimethylcyclohexane to ten deuterium atoms (the number of hydrogen atoms attached to the ring) illustrates the same point (Table I, run 21a). These runs show however, that the double branch does not seriously interfere with exchange of the hydrogen atoms attached to the carbon atom adjacent to the branch.

Neopentane (Table I, run 15a) exchanges very slowly. The principle species which appears is $C_5H_{11}D$. Concentrations of doubly and trebly exchanged species are small. Therefore, α - α migration of the position of attachment is not very frequent.

α - δ migration is also infrequent. It hardly occurs at all past a double branch as shown by 3,3-dimethylpentane and 1,1-dimethylcyclohexane. Were it to occur with cyclohexane exclusively, then only the six hydrogen atoms attached to carbon atoms 1 (the atom at which adsorption first occurs) 3 and 5 would exchange. The complete absence of any anomaly in the concentration of $C_6H_6D_6$ proves that this reaction is not the major one. (Table I, run 18a, Table II, run 144).

On the other hand, as shown by multiple exchange in 3,3-dimethylpentane, α - β migration occurs. It seems likely, then, that α - β migration is the reaction which is principally responsible for multiple exchange.

If cycloalkanes were adsorbed flat, one would expect an anomaly to appear at the concentration of the species in which half of the hydrogen atoms in the ring were exchanged. No such anomaly appears in cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane or dimethylcyclohexane. Furthermore, one might expect hindrance to the flat adsorption of the last hydrocarbon, but its exchange pattern closely resembles that of cyclohexane.

The migration of the position of attachment in cyclic systems

is relatively stereo-insensitive. Thus, if migration were to occur exclusively to an adjacent cis-position, cyclopentane and cyclohexane would exchange but half of their hydrogen atoms. If migration were to occur exclusively to the trans-position, cyclohexane would exchange but six hydrogen atoms.

Furthermore, migration of the point of attachment does not require that the hydrogen atom adjacent to the point of attachment to be in a gauche-or a trans-position since the rigid molecule, cyclopentane, exchanges without difficulty.

The exact shape of the exchange distribution pattern varies among the four types of nickel catalysts which we have studied. With heptane and 3-methylhexane, evaporated nickel and reduced nickel oxide give pronounced maxima in the concentration of the multiply exchanged species. A minimum occurs amongst those species with triple to sextuple exchange (Table I, runs 5, 10, 13a, 19; Table II, runs 122, 136, 137, 150, 153). The nickel kieselguhr previously studied² gave a slight maximum with 3-methylhexane but in heptane, the maximum became a long flat portion (Table II, runs B23 and B115). The Harshaw nickel-kieselguhr exhibits maxima with both hydrocarbons (Table II, runs 105 and 107) but the maxima are less pronounced than with evaporated nickel or reduced nickel oxide.

As deuterium accumulates in the gaseous hydrogen, one would expect the position of the maximum in the exchange patterns of 3-methylhexane and heptane to shift to species of lower exchange. On reduced nickel oxide this trend is seen in comparing the sequence of runs 122, 136 and 153 (Table II). In run 122 at 160°, in the alkane product, 2.5% of the hydrogen was substituted by deuterium, or, 13% of the hydrogen gas had become deuterium. In run 153 at 210°, the corre-

sponding figures are 7.1% and 50%. The position of the maximum is moved back in run 153 but the most extensively exchanged species (D_{14} , D_{15} , and D_{16}) are even less exchanged than the build-up of hydrogen deuteride alone would warrant. The concentrations of the last three species should be little lower in run 153 than in run 122 since subsequent exchange following the attainment of as much exchange as in run 122 was relatively uncommon. Thus, apparently, the most extensive exchange is less likely at higher temperatures. Whether this is true for evaporated nickel films is open to some doubt since partial poisoning may also affect the exchange pattern.

On the whole, evaporated nickel films and reduced nickel oxide behave very similarly. This may be seen in comparing heptane on the two catalysts (Table I, run 10a; Table II, run 124), cyclohexane (Table I, run 18a; Table II, run 144) and 3,3-dimethylpentane (Table I, run 12a; Table II, run 141) in which case the minimum at $C_5H_{10}D_2$ occurs in both runs. There is no sign of anything unusual about evaporated nickel films. Once this material has been exposed to reactant it behaves in a standard fashion.

Oriented nickel films prepared by evaporation in 1 mm. of nitrogen rather than in vacuo gave exchange patterns with 3-methylhexane and with cyclopentane which were of the same general type as those of unoriented films. Comparison of runs 22a and 22b with 19a and 19b and of 22c with 16b demonstrate this point. The oriented film was, however, much more active than any other films both absolutely and relatively since its weight was but about a fifth that of the unoriented films. As will appear, the ratio of exchange to racemization with (+)3-methylhexane was also the same as with unoriented films. Oriented films are more active in ethylene hydrogenation than are unoriented ones.⁸

The difference between these two catalysts and the nickel-kieselguhr ones seems to be that the relative probability of the propagation reaction versus the evaporation reaction is greater for the first two catalysts. We suggest tentatively that this is correlated with particle size, being greater on the material of larger crystallite size. The former nickel-kieselguhr catalyst shows a variation of magnetization with temperature² indicative of small particle size.⁹

(9) P. W. Selwood, T. R. Phillips and S. Adler, J. Am. Chem. Soc.,
76, 228 (1954).

The plot of magnetization against temperature for the reduced nickel oxide is very similar to that of bulk nickel.¹⁰ This is

(10) We are indebted to Dr. T. R. Phillips for this determination.

indicative of relatively large particle size. A sample of nickel-kieselguhr which had been reduced at 250° gave an exchange pattern with 3-methylhexane corresponding to nearly exponential decline (Table II, run B17) with increasing deuteration. Such a catalyst would be expected to have a smaller particle size than a catalyst reduced at 300°.⁹

Leaving out of consideration the blocking of the propagation reaction, the exchange patterns fall into two groups as shown in Fig. 1. 3-Methylhexane resembles heptane (curve A) while all the cycloalkanes resemble 2,3-dimethylbutane (curve B). The difference must lie in variation in the ratio of the probability of the propagation reaction to that of desorption. This ratio may also depend upon whether the position of adsorption is in the center or at the end of the acyclic alkanes. However, it is the more compact molecules which give the curve with the maximum at the most exchanged species. This

would seem to result from surface steric requirements for completion of the propagation reaction. (Compare, for example, 3-methylhexane and methylcyclohexane).

One might suggest that multiple exchange results from diffusion of an alkane molecule into a pore in which it has many chances of adsorption with single exchange before it diffuses out of the pore. The possibility of this kind of a diffusion mechanism is often very difficult to eliminate. It can be eliminated unequivocally in the present case. If such a mechanism were to obtain, at low total conversions at least ten hydrogen atoms of 3,3-dimethylpentane would be subject to exchange instead of but five.

One expects hydrogenolysis of carbon-carbon bonds at temperatures somewhat above those at which exchange starts.^{11,2} We passed heptane

(11) K. Morikawa, W. S. Benedict and H. S. Taylor, J. Am. Chem. Soc.,
58, 1445 (1936); 58, 1795 (1936). K. Morikawa, N. R. Trenner and
H. S. Taylor, ibid., 59, 1103 (1937).

and light hydrogen over two different freshly evaporated nickel films at 200°. The infrared adsorption spectra of the products were indistinguishable from those of the reactant. As tested mass spectroscopically no significant amount of methane appeared in the off gas. With cyclohexanes and cyclopentanes, hydrogenolysis would lead to species of mass numbers greater than those of the fully exchanged alkanes. None was observed.

With ethylcyclobutane, however, species heavier than C₆D₁₂ were observed (Table I, run 23b). D₁₃, D₁₄, D₁₅ and D₁₆ must correspond to exchanged hexanes. Thus, exchange of the cyclobutane ring is

accompanied by extensive ring opening to produce mainly 3-methylpentane.¹²

(12) V. Haensel and V. N. Ipatieff, ibid., 68, 345 (1946).

On the other hand, the peak corresponding to D₁ must be singly exchanged ethylcyclobutane. If one allows that hydrogenolysis of the ring would necessarily introduce at least two deuterium atoms, then D₂ and D₃ are doubly and trebly exchanged ethylcyclobutane. Whether these one, two and three deuterium atoms are in the ring or in the ethyl side chain could not be ascertained.

By the use of optically active 3-methylhexane, one may determine the stereochemistry of the exchange reaction. If both the production of exchanged species and the loss of rotation proceed as first order reactions, the ratio of the rate of exchange to that of racemization is

$$\ln Z / \ln (\alpha / \alpha_0)$$

where Z is the fraction of molecules which have suffered no exchange.² Table IV presents the results obtained in the present work. The probable error when small is determined by the % exchange, when larger, by the accuracy of polarimetry.

On the Universal Oil Products Company nickel-kieselguhr used before² the ratio was about 1.6, in agreement with that on the Harshaw catalyst. The reduced nickel oxide and particularly the evaporated films give lower values, closer to 1.2. With all catalysts there are some species with but a few deuterium atoms introduced in which exchange has probably not propagated to the optical center and, therefore, has not resulted in loss of rotation. The fraction of molecules having 3 deuterium atoms or less is listed in Table IV. The choice of 3 deuterium atoms is, of course, rather arbitrary.

TABLE IV
 Ration of Rate of Exchange to that of Racemization for
 (+)3-Methylhexane

Catalyst	Run no.	Ratio ^a	Fraction D ₁ +D ₂ +D ₃ ^b
Harshaw nickel-kieselguhr	107	1.7±0.1	0.24
Reduced nickel oxide	122	1.4±0.3	0.24
	136	1.6±0.2	0.21
	153	1.2±0.1	0.16
Evaporated nickel film	19a	1.1±0.1	0.12
	19b	1.5±0.3	0.19
	22a	1.1±0.1	0.08
	22b	1.2±0.1	0.12

^aThe ratio of the rate of formation of exchange species to the of loss of rotation.

^bFraction of total molecules exchanged which had 1,2 or 3 D-atoms.

The assumption that such molecules are responsible for the ratio exceeding 1.0 is consistent with the exchange patterns. There are relatively more slightly exchanged molecules with nickel-kieselguhr than with the other catalysts. Run B17, Table II, is from ref. 2 and is on a nickel-kieselguhr which had been reduced at 250° rather than at 300°. Here α/α_0 was 0.979, whence the ratio is 3.2 ± 0.6 . On this run, there is nearly an exponential decline in concentration with increasing degree of exchange and a much larger proportion of slightly exchanged species.

Our previous conclusion that racemization accompanied substantially all of the exchange at the tertiary carbon atom applies also to the catalysts studied in this paper.

A study of isotopic interchange between deuterium and ethane¹³

 (13) J. R. Anderson and C. Kemball, Proc. Roy. Soc. (London) 223A,
 361, (1954).

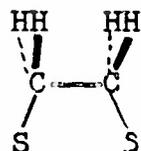
and between deuterium and propane and isobutane¹⁴ on a series of

 (14) C. Kemball, ibid., 223A, 377 (1954).

evaporated metal films including nickel has been reported. Multiple exchange was observed but, with nickel at 0° and long contact times, considerably less multiple exchange was observed than with the hydrocarbons we have studied at higher temperatures. Whether this difference results from the differences in the hydrocarbons or in the differences in temperature and pressure (Anderson and Kemball worked at much lower total pressures) is not clear. In contrast to our results, oriented and unoriented nickel films give rather different types of exchange patterns with ethane, the oriented film giving less multiple exchange.

These workers observed the degree of multiple exchange to vary considerably from metal to metal. In view of the systematic variation which we have observed among nickel catalysts and which may be correlated with crystallite size, the variations observed from metal to metal may not depend solely on the identity of the metal.

Kemball and Anderson interpreted multiple exchange by the same general type of process which had been suggested for rickel-kieselguhr.² However, their suggestion that the propagation of the exchange reaction proceeds through



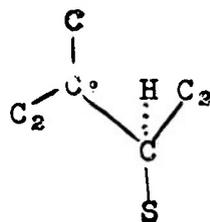
suffers from the difficulty that it cannot explain the racemization of (+)3-methylhexane.² Further, it is equivalent to adsorbed ethylene, which, in the presence of deuterium, returns considerable deuterio-ethylene to the gas phase as is also true of adsorbed butylenes.¹⁴

(14) T. I. Taylor and V. H. Dibeler, J. Phys. Colloid Chem., 55, 1036, (1951). This paper is a leading reference to previous work in the field of olefin hydrogenation and exchange.

One would have to assume that no such return would occur in exchange between alkanes and deuterium since, at the temperatures under consideration, the equilibrium concentration of olefin would be infinitesimal. Similar objection can be raised to two of the symmetric intermediates suggested to allow for racemization.² This argument alone is not necessarily fatal since the rate of olefin desorption could vary with surface conditions as influenced by the partial pressure

of olefin in the vapor phase.

One symmetric intermediate previously suggested² could account for the results and would confine the propagation reaction to an α - β shift. As applied to (+)3-methylhexane it takes the form



On the other hand, an adsorbed alkyl group might have a less classical structure. Our knowledge of surface orbitals does not seem adequate to specify exactly the nature of an adsorbed radical. If the adsorbed alkyl group was planar and if the plane of the radical



was perpendicular to the surface, adsorbed (+)3-methylhexane would pass through a symmetric form. The details of the exchange of cycloalkanes would also be intelligible. This proposed intermediate is equivalent to a free radical in which the p -orbital interacts with surface orbitals. Addition of a hydrogen atom to the central carbon atom would result in desorption while simultaneous removal of a hydrogen atom from one of the adjacent carbon atoms would result in propagation of exchange. However, the stereochemistry would be satisfied if the adsorbed alkyl group merely passed through the proposed structure. The adsorbed alkyl group would not necessarily exist mainly in such a form.

We have derived an expression for the exchange pattern of cyclopentane on a model involving initial adsorption at a single point coupled with random migration of this point of attachment with exchange of a deuterium atom at each shift. This model does not confine the propagation reaction to α - β shifts but mathematically it is less refractory.¹⁵ When probability of migration of the point

(15) We are indebted to Mrs. H. C. Rowlinson for the mathematical
solution of this combinatorial problem.

of attachment at any stage is about 0.91 (or the probability of desorption is 0.09), the exchange pattern is one in which all exchanged species have about the same concentration. When the migration probability exceeds 0.91, the concentration steadily increases with increasing exchange, and when it is less than 0.91 it declines with increasing exchange. The exchange pattern of cyclopentane cannot result from such a model. However, if the migration probability was below 0.9 on one crystal face and above 0.93 on another face, then a curve of the observed form (Table I, run 16b) would result. Anderson and Kemball¹² treated ethane from a rather similar model with similar conclusions. In any case, considering that many of the exchanges accompanying the propagation reaction would merely replace a deuterium atom by another deuterium atom, the net probability of desorption at any stage must be small in order that exchange of all hydrogen atoms in a substantial fraction of cyclopentane would result.

Acknowledgment.— This research was supported by the Office of Naval Research. One of us, Richard H. Tuxworth, was the holder of a Visking Corporation Fellowship.

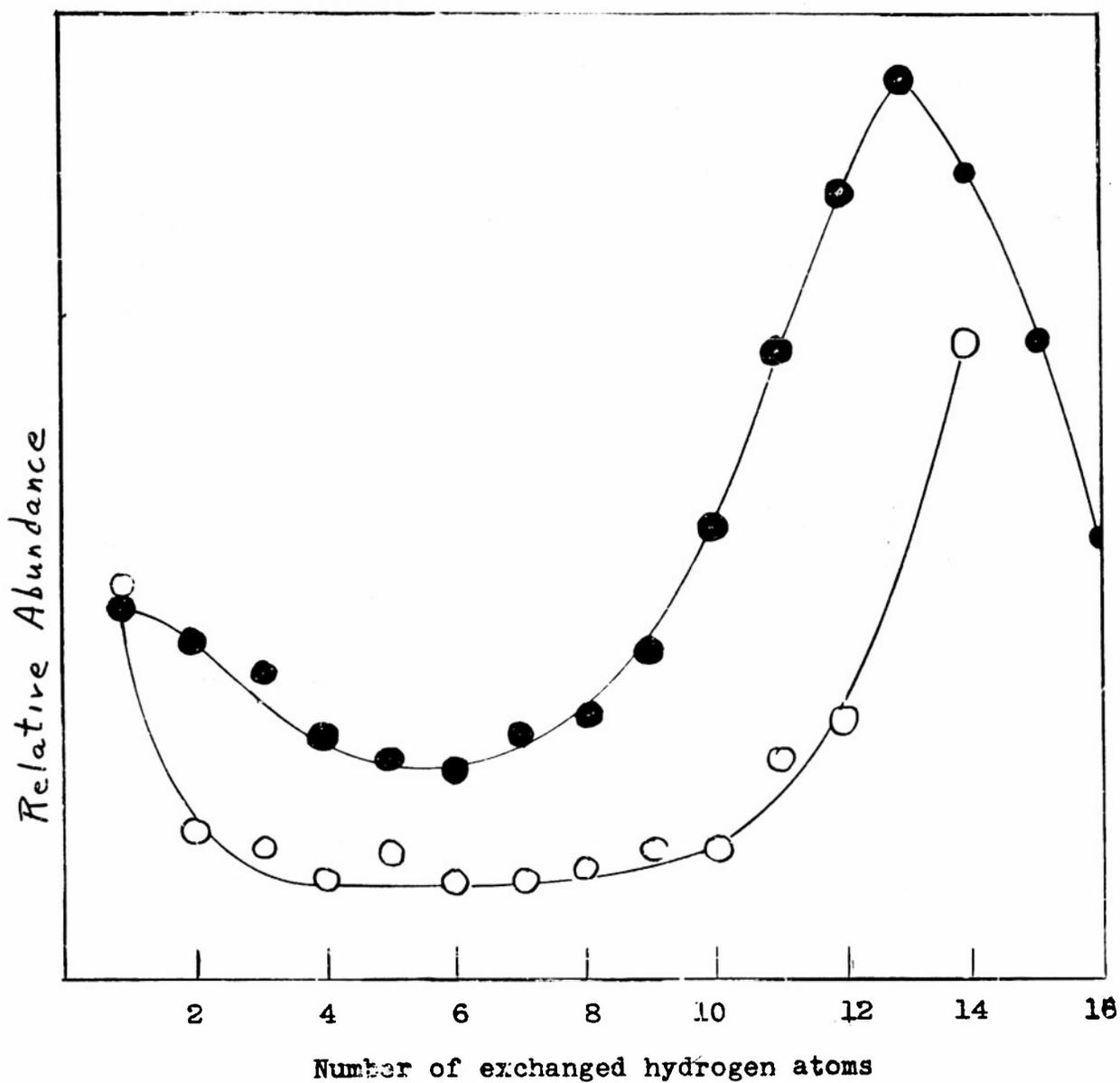


Fig. 1 Relative abundances of exchanged species with heptane, run 10a, ●●●, and 2,3-dimethylbutane, run 13b, ○○○.

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