The integral distribution curve for the 10 mole % copolymer is shown on Fig. 6. The value of $M_0$ for the $n = 0.5$ curve (equation 3) was calculated from the value of $[\eta]_0$ in Fig. 5. The other two theoretical distribution curves were computed from equation 3[21] by selecting values of "$M_0$" which caused all three curves to coincide at $W(M) = 50\%$. Inspection of the figure again shows that the distribution approximates the most probable distribution, for which case Stockmayer's[2] calculations were made.

In conclusion, it may be stated that the composition distribution of the above copolymers is within the experimental error of that predicted by Stockmayer's statistical analysis, thus demonstrating that polymerizations by the organometallic mixed catalysts are amenable to the same kinetic and statistical treatments that have been applied to the classical catalysts. The uniformity of the copolymers prepared by the soluble, $AlBr_3$–$VX_n$–$Sn(C_6H_5)_4$, catalyst strongly supports the view that the heterogeneous copolymers usually prepared by the mixed catalysts are due to a multiplicity of active sites. Obviously, the relative concentrations of the various sites will depend on the specific catalyst formulation techniques employed; therefore, for these mixed catalysts, quantitative comparison of copolymerization kinetic data from different sources will be difficult unless detailed composition distributions are routinely included along with the reactivity ratio values, and care is taken to insure that only one active species is present.[23]

**Acknowledgments.**—We wish to thank Dr. A. K. Ingberman and Mr. R. J. Turbett for the $TiCl_4$–$(C_2H_5)_3Al$ copolymer. We are particularly indebted to Dr. G. E. Myers for many discussions on and considerable assistance with the elution fractionation.

[23] This work was presented at a Symposium at Polytechnic Institute of Brooklyn, April 29, 1961. At the same Symposium, C. A. Lukach also presented a paper showing a narrow composition distribution in copolymers (approximately 30 mole % propylene) prepared with aluminum alkyl + alkyl vanadate catalysts, and G. Bier, *Angew. Chem.*, **73**, 186 (1961), also has recently reported that vanadium catalysts are more homogeneous than titanium catalysts.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

# Reactions between Deuterium and Olefins in the Liquid Phase on Platinum Oxide Catalysts[1]

BY GERARD V. SMITH AND ROBERT L. BURWELL, JR.[2]

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The liquid phase deuterogenation of 1-hexene, $\Delta^{1,9}$- and $\Delta^{9,10}$-octalin on platinum oxide catalysts has been investigated at room temperatures in the liquid phase. The deuterogenation of 1-hexene is accompanied by isomerization to *cis*- and *trans*-2-hexene at a rate 3% of that of deuterogenation and by formation of deuteriated hexene of which 90% is 1-hexene at a rate 30% of that of deuterogenation. Most of the saturated product consists of hexane-$d_0$ to -$d_6$ with $d_{av.}$ about 2.0. Similar isotopic distribution appears in the decalins produced from $\Delta^{1,9}$-octalin (54% *cis*-, 46% *trans*-decalin). Exchanged $\Delta^{1,9}$-octalin is formed but no isomerized octalins. These data appear consistent with adsorption of olefin as a *vic*-diadsorbed species, conversion to mono-adsorbed alkane followed by alternation between mono- and diadsorbed alkane. Isotopic exchange between surface H-atoms and gas phase deuterium is slow relative to desorption of monoadsorbed alkane. $\Delta^{9,10}$-Octalin can be hydrogenated only by adding acetic acid or by prereducing the catalyst in dilute acid. In the latter case the product is 61% *cis*- and 39% *trans*-decalin, reaction is slow and $d_{av}$ is nearly 3.0. In all of the *trans*- and 85% of the *cis*-decalin, at least three hydrogen atoms have been equilibrated with the surface H,D-atom pool in contrast to the situation with $\Delta^{1,9}$-octalin where only two hydrogen atoms have been equilibrated in 75% of the product decalins. Most of the *cis*- and all of the *trans*-decalin produced from $\Delta^{9,10}$-octalin appear to be derived from a common intermediate in which three hydrogen atoms are equilibrated, possibly $\Delta^{1,9}$-octalin-10-*d*.

Although our understanding of the mechanistic details of heterogeneous catalytic reactions remains seriously inadequate, substantial advances have been made recently toward a reasonably satisfactory mechanistic interpretation of heterogeneous catalytic reactions between hydrogen and hydrocarbons in the vapor phase. This work constitutes a development and extension of the classical Horiuti–Polanyi mechanism for olefin hydrogenation, and it has come from studies involving isotopic tracers, stereochemistry and variation in hydrocarbon structure rather than from mere kinetics. References to reviews of this work are given in the footnotes.[3–5]

This theory would represent reactions among butylenes, butane and hydrogen as shown in Fig. 1.[6] Catalytic sites on the metallic surface are indicated by asterisks. To simplify the diagram, hydrogen atoms attached to surface sites, *-H, have been omitted. The stereochemistry and geometric arrangement at the carbon atoms bonded to the surface in *vic*-diadsorbed butanes (II, V, VI)[7] appears to resemble that of eclipsed ethanes.[5,7]

Mere hydrogenation of 1-butene occurs by the sequence I, II, III, IV. Isomerization of 1- to *trans*-2-butene, for example, can occur *via* the sequence I, II, III, V, VIII.

In Fig. 1, 2-monoadsorbed butane[7] (III) and 3-monoadsorbed butane (IX) are identical as are the two butanes, IV and X. Substitution of deute-

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[1] Supported by U. S. Army Research Office (Durham).

[2] To whom communications concerning this paper should be addressed.

[3] T. I. Taylor in "Catalysis," edited by P. H. Emmett, Reinhold Publishing Corporation, Vol. V, New York, N. Y., 1957, Chapt. 5.

[4] C. Kemball, *Advances in Catalysis*, **11**, 223 (1959).

[5] (a) R. L. Burwell, Jr., *Chem. Revs.*, **57**, 895 (1957). (b) *Rev. inst. franç. pétrole*, **15**, 145 (1960).

[6] See, for example, G. C. Bond and J. Turkevich, *Trans. Faraday Soc.*, **49**, 281 (1953).

[7] R. L. Burwell, Jr., B. K. C. Shim and H. C. Rowlinson, *J. Am. Chem. Soc.*, **79**, 5142 (1957). A description of the nomenclature of adsorbed species appears on p. 5145.

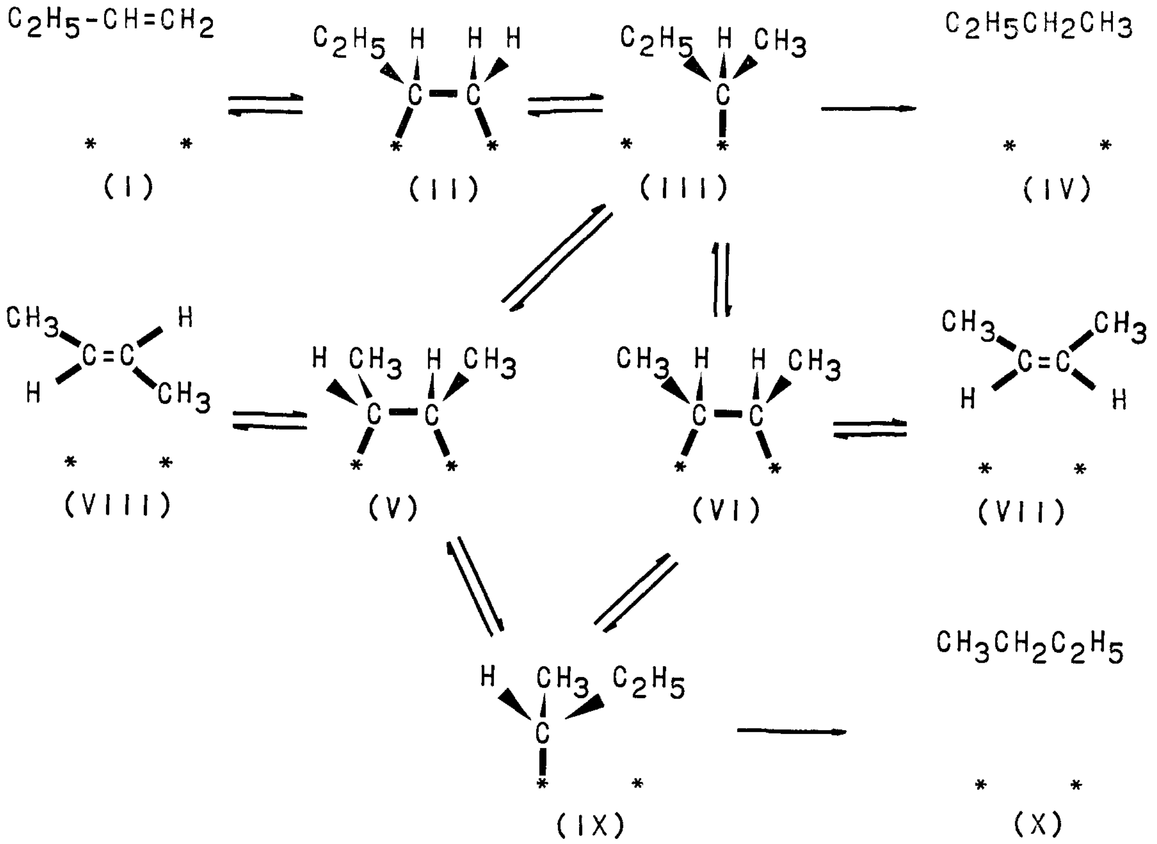
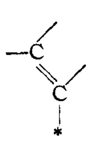


Fig. 1.—Extension of Horiuti–Polanyi mechanism as applied to butylenes.

rium for hydrogen causes the species to become different. Thus, the sequence I, II, III, IV gives 1,2-dideuteriobutane, whereas I, II, III, V, IX, X gives 1,2,3-trideuteriobutane. Alternation among mono- and diadsorbed species can lead to any degree of deuteriation in product butane including that of perdeuteriobutane.

In addition to monoadsorbed alkane and *vic*-diadsorbed alkane, some symmetric adsorbed species is required in isotopic exchange experiments which can cause racemization of optically active hydrocarbons during exchange and permit the carbon-surface bond in species such as monoadsorbed cyclopentane to shift from one side of the ring to the other. A possible species is an α-monoadsorbed olefin.[5,7]



(XI)

The mechanistic considerations given above have developed nearly exclusively from studies of vapor phase reactions. Such reactions have certain advantages for mechanistic studies: complications from diffusional control can be recognized better and eliminated,[8] activity coefficients can be taken as unity at ordinary pressures, and solvent effects do not enter. On the other hand, many data on liquid phase hydrogenations exist and require interpretation, one can work with a much wider variety of hydrocarbon structures in the liquid phase than in the vapor phase, and solvent effects may turn out to be mechanistically revealing rather than confusing.

In addition, one may note that many investigators of liquid phase hydrogenation reactions have ignored the results of vapor phase studies and have implicitly assumed that the two types of reactions are inherently different. For example, mechanisms of hydrogenation have been proposed which would be very improbable in vapor phase reactions.

We report here an extension to liquid phase systems of the type of study which had been carried out in vapor phase reactions. The addition of of deuterium to 1-hexene is of a type which has been studied in the vapor phase. The addition of deuterium to $\Delta^{9,10}$-octalin represents a reaction which would be difficult to study in the vapor phase because the vapor pressure of the octalin is too low at temperatures of interest. It was chosen for stereochemical reasons. The scheme of Fig. 1 leads to *cis*-addition to an olefin, and, of all olefins, one might think that $\Delta^{9,10}$-octalin would be that one most likely to reveal pure *cis*-addition. However, several investigators have reported that one gets about equal quantities of *cis*- and *trans*-decalins.[5a,9] *trans*-Decalin might result by preliminary isomerization to $\Delta^{1,9}$-octalin which can undergo *cis*-addition of hydrogen atoms to give either *cis*- or *trans*-decalin, or it might result

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[8] R. Ciola and R. L. Burwell, Jr., *J. Phys. Chem.*, **65**, 1158 (1961).

[9] J.-F. Sauvage, R. H. Baker and A. S. Hussey, *J. Am. Chem. Soc.*, **82**, 6090 (1960).

from isomerization of adsorbed *cis*-decalin *via* an adsorbed species analogous to α-monoadsorbed olefin (XI and XIV). We hoped that a detailed analysis of the deuterogenation reaction might help in determining the over-all mechanism.

We have employed the Adams platinum catalyst because of the large amount of descriptive work which has used it. As will appear, it is not an ideal catalyst for such a study because of variations in its catalytic characteristics and because of a tendency to clump during reaction.

## Experimental

**Materials.**—Hexene-1, Phillips pure grade, was redistilled and stored in a brown bottle under nitrogen. $\Delta^{9,10}$-Octalin was prepared by a method suggested by Dr. Allen S. Hussey which we believe to be much better than any previously described. β-Naphthol was hydrogenated over nickel-kieselguhr at 150° and 10 atmospheres pressure. The resulting mixture of β-decalols and decalins (which resulted from hydrogenolysis) was dropped into 100% phosphoric acid at 150° to give a mixture of octalins plus contaminating decalins. The octalin fraction of $\Delta^{9,10}$ was about 78%, of $\Delta^{1,9}$, about 17%. The other octalins were present in few % quantities. The entire mixture was selectively hydrogenated over reduced platinum oxide at room temperatures and a pressure of two atmospheres. Those octalins which were present in small quantities and which are di-substituted ethylenes reacted first. When they had disappeared, the $\Delta^{1,9}$-octalin (a tri-substituted ethylene) reacted. Hydrogenation was interrupted when it had disappeared. The resulting mixture of $\Delta^{9,10}$-octalin and decalins was run into a 5.5-ft. column of silica-gel and eluted with pentane. The $\Delta^{9,10}$-octalin was isolated in a purity of 99.9% as judged by gas chromatography.

$\Delta^{1,9}$-octalin was isolated in pure form from a mixture of it and *trans*-$\Delta^{1,2}$-octalin, which had been prepared by pyrolysis of the acetate of *trans*–*cis*-α-decalol. We are indebted to Dr. Allen S. Hussey for supplying us with this mixture. It was selectively hydrogenated and chromatographed on silica-gel with the help of Mr. E. F. Meyer.

Hexane was Phillips pure grade. Glacial acetic acid was purified by refluxing over chromic oxide followed by distillation. Hydrogen (Matheson electrolytic) and deuterium (Stuart Oxygen Company) were passed through a Deoxo unit and a trap containing Drierite. Platinic oxide was secured from the American Platinum works.

**Apparatus.**—The hydrogenation apparatus provided the following features: small scale because of considerations of cost, agitation adequate to suspend the catalyst in the liquid medium, effective equilibration of the gas and liquid phases and good mixing of the entire deuterium phase (in the event that isotopic exchange released hydrogen into the gas phase deuterium).

The reaction chamber was of tubing with an inside cross-sectional area of 1.1 sq. cm., joined at the bottom to 2 mm. capillary tubing. A fritted glass disk about 6 mm. in diameter was sealed into the conical portion which joined the capillary to the reaction chamber. A peristaltic action pump circulated deuterium up through the fritted disk at a rate of about 65 cc. per min. The resulting bubble stream rising through the liquid–catalyst mixture in the reaction chamber kept the catalyst suspended and provided good contact between liquid and gas. The tubing above the reaction chamber was cooled first at 0° and then at −78° to strip the deuterium gas flow of vaporized hydrocarbon. The deuterium passed then into a large ballast bulb and thence through a charcoal trap cooled with liquid nitrogen back to the pump. Olefin was introduced and samples were removed for analysis through a serum cap fitted at the top of the reaction chamber.

Weighed catalyst was placed on top of the fritted disk and the system was evacuated for 1 hr. Hydrogen or deuterium then was slowly allowed to enter the system *via* the liquid nitrogen trap, bulb and condenser train. The catalyst was reduced during the earlier stages of this process. Since considerable heat is liberated the initial portions of hydrogen were introduced very slowly.[10] Hydrogen admission was stopped at a total pressure of one atmosphere and the hydrogen was circulated through the system for fifteen minutes to remove water formed by reduction. Reaction was started by injecting the liquid phase into the reaction chamber. Rates of reaction were followed by a mercury manometer.

The free volume of the system was 3.6 l. About 0.01 g. of catalyst and 1 cc. of olefin were employed. The mole ratio of deuterium to olefin was usually greater than 20 so that effects of any isotopic dilution were small.

**Analysis.**—Hexene–hexane mixtures were analyzed by gas chromatography on a 14-ft. tricresyl phosphate column; the octalin–decalin mixtures, on a 20-ft. LAC446 (Aerograph) column with helium as the carrier gas. The products of hexene hydrogenation were analyzed for isotopic content on a manual Westinghouse instrument in our Department of Chemical Engineering. The octalin analyses were performed on a Consolidated instrument at the Institute of Gas Technology, Chicago. Procedures followed those previously used.[6,11] In certain cases, reaction mixtures were separated by gas chromatography before analysis.

**Rates of Reaction.**—Our kinetic data were obtained mostly as an accompaniment to other determinations. Rates of hydrogen absorption were independent of time. Hence, the hydrogenations were zero order in olefin and no poisoning occurred during the course of reaction. Changes in total hydrogen pressure were only about 5%, and we worked only at 1 atm. so that we could not determine order in hydrogen. By analogy with many previous kinetic investigations, we assume that order in hydrogen is unity. Transfer of hydrogen between gas and liquid phase does not appear to be controlling (*i.e.*, the liquid phase always is nearly saturated with respect to hydrogen), since the rate of hydrogenation of a fixed quantity of 1-hexene is proportional to catalyst weight[12] to within catalyst reproducibility in the range 0.01 to 0.02 g. In addition, different conditions of pre-treatment produce different rates. Treatment of the reduced catalyst at 250° *in vacuo* lowered the reaction rate to 1/14th of the standard. Preevacuation of the unreduced catalyst (run 9) raised the rate by a factor of 1.6.

The standard rate of hydrogenation of 1-hexene at 24.5° was 0.016 mole of hydrogen per gram of catalyst per minute. To within the reproducibility of rates, about ±15%, rates of reaction of hydrogen and of deuterium were identical.

**Hydrogenation of 1-Hexene.**—Gas chromatographic analysis of hydrogenations or deuterogenations of 1-hexene at various stages are given in Table I. The tricresyl phosphate gas chromatography column would not clearly separate 3-hexenes from 2-hexenes. Accordingly, runs 10 and

TABLE I

HYDROGENATION OR DEUTEROGENATION OF 1-HEXENE

| | | % | | | |
|---|---|---|---|---|---|
| Expt. no. | Reductant | Hexane | 1-Hexene | *Trans*-2-hexene | *Cis*-2-hexene |
| 15a | $D_2$ | 12.5 | 86.9 | 0.3 | 0.2 |
| 12a | $H_2$ | 18.8 | 80.0 | .6 | .5 |
| 12b | $H_2$ | 41.4 | 57.3 | .7 | .6 |
| 15b | $D_2$ | 43.1 | 55.5 | .7 | .6 |
| 11[a] | $D_2$ | 60.1 | 37.8 | 1.1 | .9 |
| 10 | $H_2$ | 67.5 | 31.9 | 0.7 | .6 |
| 14b | $D_2$ | 86.5 | 10.7 | 1.8 | 1.0 |
| 13c | $D_2$ | 94.0 | 3.8 | 1.4 | 0.8 |
| 12c | $H_2$ | 97.1 | 0.4 | 1.6 | .9 |
| 9 | $H_2$ | 100.0 | .0 | 0.0 | .0 |
| 14c | $D_2$ | 100.0 | .0 | .0 | .0 |
| 31a[b] | $D_2$ | 38.1 | 61.5 | .25 | .15 |

[a] Catalyst clumped and gave but $^1/_3$ standard rate. Probably the catalyst was reduced too fast. [b] Catalyst pre-reduced in dil. HCl.

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(10) Some difficultly reproducible loss in catalytic activity is apt to occur during this step. Catalyst could not be introduced after hydrocarbon had been added because evolved water usually causes the catalyst to clump in the presence of liquid in which water is insoluble. If the platinum oxide is evacuated for four days before use, initial catalytic activity is about 1.6 times greater than usual (Table I, run 9). The oxide visibly changes color and perhaps evolves oxygen with consequent lowering of the final heat of reduction and ensuing sintering.

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

(12) H.-C. Yao and P. H. Emmett, *ibid.*, **81**, 4125 (1959).

TABLE II

ISOTOPIC ANALYSIS OF SEPARATED DEUTEROGENATION PRODUCT

| Mass no. | Separated hexene, % | Separated hexane, % | Total mixture, % |
|---|---|---|---|
| 84 | $d_0$ 85.0 (86.7) | | ene-$d_0$ 90.9 |
| 85 | $d_1$ 10.0 (10.2) | | ene-$d_1$ 9.1 |
| 86 | $d_2$ 2.6 ( 2.5) | $d_0$ 10.6 (11.3)[a] | ane-$d_0$ 12.0 |
| 87 | $d_3$ 1.3 ( 0.6) | $d_1$ 35.5 (22.6) | ane-$d_1$ 34.8 |
| 88 | $d_4$ 0.5 ( .0) | $d_2$ 34.5 (20.9) | ane-$d_2$ 34.1 |
| 89 | $d_5$ .4 ( .0) | $d_3$ 11.9 (11.9) | ane-$d_3$ 11.6 |
| 90 | $d_6$ .2 ( .0) | $d_4$ 4.8 ( 4.7) | ane-$d_4$ 5.0 |
| 91 | | $d_5$ 1.9 ( 1.3) | ane-$d_5$ 1.9 |
| 92 | | $d_6$ 0.5 ( 0.3) | ane-$d_6$ 0.3 |
| 93 | | $d_7$ 0.4 | ane-$d_7$ 0.3 |
| Av. D atoms in hydrocarbon | 0.24 (0.17) | 1.75 | 1.71 |

[a] The figures in parentheses represent the random distribution for a deuterium content of 1.75, multiplied by 0.73 so as to make $d_0$, $d_3$ and $d_4$ nearly in agreement with experiment.

TABLE III

ISOTOPIC ANALYSES OF DEUTEROGENATION RUNS

| Run no. | 15a | 14a | 13b | 31b | 14b | 13c | 14c | 31c |
|---|---|---|---|---|---|---|---|---|
| Hexane, %[a] | 10.2 | 25.6 | 41.8 | 68.3 | 85.7 | 93.7 | 100.0 | 100.0 |
| ene-$d_0$, % | 97.0 | 91.9 | 89.7 | 79 | 76 | 70 | | |
| ene-$d_1$, % | 3.0 | 8.1 | 10.3 | 21 | 24 | 30 | | |
| ane-$d_0$, % | 15.0 | 13.5 | 11.8 | 16.1 | 10.1 | 9.7 | 8.8 | 10.8 |
| ane-$d_1$, % | 35.5 | 35.2 | 34.2 | 35.1 | 32.8 | 33.9 | 31.1 | 31.8 |
| ane-$d_2$, % | 29.5 | 31.1 | 34.0 | 29.5 | 34.4 | 33.8 | 34.2 | 31.3 |
| ane-$d_3$, % | 10.7 | 10.7 | 12.4 | 12.1 | 14.2 | 13.9 | 14.8 | 14.4 |
| ane-$d_4$, % | 4.6 | 5.5 | 4.5 | 4.3 | 5.5 | 5.7 | 6.6 | 6.7 |
| ane-$d_5$, % | 3.4 | 2.0 | 1.7 | 1.7 | 2.2 | 1.7 | 2.7 | 2.7 |
| ane-$d_6$, % | 0.9 | 1.4 | 0.9 | 0.6 | 0.6 | 0.7 | 1.1 | 1.2 |
| ane-$d_7$, % | .5 | 0.8 | .3 | .2 | .4 | .6 | 0.5 | 0.5 |
| ane-$d_8$, % | .0 | 0.0 | .0 | .1 | .0 | .0 | 0.2 | .26 |
| ane-$d_9$, % | | | | .09[b] | | | | .17[c] |
| Av. D. content | 1.71 | 1.76 | 1.73 | 1.65 | 1.84 | 1.83 | 1.96 | 1.95 |

[a] % Hydrogenation determined mass spectrographically. [b] Runs 31b and 31c were analyzed on the Consolidated instrument, which has a sensitivity about ten times that of the Westinghouse (0.01–0.02% *vs.* 0.1–0.2%). Hexane-$d_{10}$, 0.07%; $d_{11}$, 0.05; $d_{12}$, 0.05; $d_{13}$, 0.03; $d_{14}$, 0.02. [c] Hexane-$d_{10}$, 0.11%; $d_{11}$, 0.06; $d_{12}$, 0.02; $d_{13}$, 0.01; $d_{14}$, 0.01.

11 were analyzed on silver nitrate–glycol columns which would separate all five hexenes. The content of *trans*-3-hexene, if any, was less than 10% of that of *trans*-2-hexene. The more convenient tricresyl phosphate column was used for the other hexene runs.

After investigation of deuterogenation of octalins, catalyst which was prereduced in dilute hydrochloric acid was tested for hexene deuterogenation, Table I, run 31. This catalyst was evacuated for ten days after insertion in the hydrogenation apparatus. The rate of hydrogenation was about 1.15 times that of the standard catalyst. Except that the relative rate of isomerization was definitely less, the pre-reduced catalyst behaved much like the standard catalyst.

Table II gives the isotopic analysis of run 15b of Table I, which was 43.1% hydrogenated. The product was separated by gas chromatography into hexane and total hexene and both fractions were analyzed by mass spectroscopy. In addition, the total product was analyzed without separation, in which case there is no unequivocal way of dividing mass number 86 into hexene-$d_2$ and hexane-$d_0$, mass number 87 into hexene-$d_3$ and hexane-$d_1$, etc. Arbitrarily, all species of mass numbers 86 and greater were assigned to hexane. Results are shown in the last column. Errors in the hexane analysis are negligible but the olefin analysis misses all hexenes more exchanged than hexene-$d_1$. However, the approximate degree of exchange of hexene is shown correctly. In the hexene analysis, the concentrations of hexene-$d_4$, -$d_5$ and $d_6$ are nearly proportional to the corresponding values for hexanes of the same mass number. Very probably, the sample of hexene was contaminated with about 1% hexane. The values in parentheses are those corrected for the maximum possible contamination.

Table III shows the mass spectrographic analyses of the total product of the other deuterogenation runs of Table I treated in the same way as in the last column of Table II. The % hexane computed from the mass spectrographic data is given in the first row.

**Hydrogenation of Octalins.**—Table IV gives results of octalin runs. $\Delta^{9,10}$-Octalin could not be reduced on the standard catalyst, catalyst A. In run 19, for example, hydrogenation was attempted without the presence of acetic acid. As no detectable hydrogenation occurred, the acetic acid was injected. The reported hydrogenation started at once. That lack of hydrogenation was not due to adventitious poisons in the octalin was shown by run 20 in which no hydrogenation occurred during a 2-hr. period although, apparently, traces of $\Delta^{1,9}$-octalin were formed. 1-Hexene then was injected. Its hydrogenation started immediately at nearly the standard rate.

Hydrogenation occurred on catalyst which was pre-reduced in 0.12 *M* hydrochloric acid, washed and evacuated for nine days. We do not know that such a long period of evacuation is essential. In run 23, evacuation was for 4 hr. Hydrogenation occurred slowly but the catalyst was clumped and clumping increased seriously with time.

TABLE IV

HYDROGENATION OF OCTALINS

| Expt. no. | Octalin[a] | Reductant | Catalyst | Solvent[b] | Rate[c] | % *cis* in decalin |
|---|---|---|---|---|---|---|
| 19 | 9,10 | $H_2$ | A | HOAc | 0.12 | 51 |
| 29 | 1,9 | $H_2$ | A | HOAc | 1.0 | 52 |
| 23 | 9,10 | $H_2$ | B[d] | None | 0.01 | 66 |
| 27 | 9,10 | $D_2$ | B | | .026 | 60.9 |
| 28 | 9,10 | $H_2$ | B[e] | | | 57.5 |
| 30 | 1,9 | $D_2$ | B | | .9 | 54 |
| 25 | 9,10 | $D_2$ | B[f] | | .064 | 46 |

[a] 0.5 cc. of octalin in all runs. [b] 1.0 cc. of hexane present except in run 23 when no diluent was used. In runs 19 and 29, 0.25 cc. of glacial acetic acid also was present. [c] Relative to standard hexene runs. Owing to much smaller number of moles of octalin than of hexene, pressure falls were small, precision was low and the entered rates are orders of magnitude only. [d] Pre-reduced catalyst evacuated but 4 hr. The catalyst was rather badly clumped. A similar run gave similar results. [e] Following run 27, the catalyst and reactor were washed twice with hexane with exclusion of air, evacuated and rerun with hydrogen. Because of unknown quantity of catalyst removed in the sampling process, no reliable rate data are available. [f] The clumped catalyst was disintegrated mechanically and washed with acetone, see text.

An evacuation period of 12 hr. also led to badly clumped catalysts in two instances. One would not cause hydrogenation of $\Delta^{9,10}$-octalin. With the idea that the clumping might be caused by water, the other was washed with acetone and disintegrated mechanically by a long, thin glass rod. The

TABLE V

ISOTOPIC ANALYSES OF OCTALIN DEUTEROGENATION

| | Expt. 25 $\Delta^{9,10}$-Octalin 81.2% reduction | | | Expt. 27 $\Delta^{9,10}$-Octalin 55.3% reduction | | | Expt. 30 $\Delta^{1,9}$-Octalin 36.6% reduction | | |
|---|---|---|---|---|---|---|---|---|---|
| No. of D atoms | ene | *cis*-ane | *trans*-ane | ene | *cis*-ane | *trans*-ane | ene | *cis*-ane | *trans*-ane |
| 0 | 81.2 (82.0) | 7.9 | 6.0 | 88.4 (88.8) | 2.9 | 2.2 | 96.3 (96.6) | 4.1 | 4.1 |
| 1 | 11.2 (11.3) | 11.9 | 11.7 | 7.6 ( 7.6) | 10.0 | 8.4 | 3.1 ( 3.1) | 22.1 | 26.9 |
| 2 | 3.6 ( 3.5) | 29.6 | 30.8 | 2.3 ( 2.3) | 31.1 | 28.6 | 0.29 ( 0.28) | 52.2 | 56.0 |
| 3 | 1.9 ( 1.8) | 29.9 | 35.2 | 0.85 ( 0.80) | 32.3 | 40.5 | .09 ( 0.04) | 14.5 | 9.5 |
| 4 | 1.3 ( 1.0) | 11.4 | 9.3 | .51 ( .36) | 13.9 | 12.2 | .11 | 4.9 | 2.4 |
| 5 | 0.51 ( 0.26) | 4.4 | 3.5 | .21 ( .03) | 4.9 | 4.2 | .05 | 1.4 | 0.68 |
| 6 | .19 ( .09) | 2.4 | 1.8 | .08 ( .01) | 2.4 | 2.0 | .02 | 0.50 | .24 |
| 7 | .06 ( .02) | 1.3 | 0.91 | .03 | 1.2 | 1.0 | .005 | .17 | .08 |
| 8 | .02 | 0.67 | .42 | .01 | 0.65 | 0.50 | | .07 | .03 |
| 9 | .01 | .30 | .18 | .003 | .36 | .26 | | .029 | .01 |
| 10 | .002 | .13 | .08 | | .20 | .13 | | .015 | .002 |
| 11 | | .05 | .03 | | .11 | .07 | | .005 | |
| 12 | | .04 | .03 | | .05 | .04 | | .004 | |
| 13 | | .01 | .01 | | .03 | .02 | | | |
| 14 | | .02 | .01 | | .01 | .02 | | | |
| 15 | | .005 | .003 | | .005 | .003 | | | |
| Av. D content | 0.337 (0.299) | 2.63 | 2.58 | 0.186 (0.163) | 2.85 | 2.85 | 0.048 (0.038) | 2.02 | 1.83 |

acetone was removed by several washings with hexane. The resulting catalyst suspended reasonably well and gave a large rate of deuterogenation (run 25, Table IV).

No significant isomerization of either octalin was detected except for the trace isomerization in run 20.

The % *cis*-decalin in total decalins given in Table IV depends in most cases upon analysis at about 50% hydrogenation. However, samples were taken at several degrees of hydrogenation in several runs. The % *cis* seems constant in the range 10–70% hydrogenation.

Three products of runs with octalins were separated by gas chromatography into starting octalin, *cis*-decalin and *trans*-decalin and analyzed mass spectrographically. Results are given in Table V. As in Table II, the octalins are probably contaminated by traces of *cis*-decalin. In Table V, the figures in parentheses which follow the octalin figures were obtained by diminishing the observed values by the maximum possible values for contamination. The correction was 1/100 of *cis*-decalin in run 25, 1/200 in run 27, and 1/420 in run 30. We believe that the parenthetical figures are substantially correct.

## Discussion

**The Deuterogenation of 1-Hexene.**—Two other reactions accompany the addition of deuterium to 1-hexene in the liquid phase on the platinum catalyst: isomerization and isotopic exchange of the olefin. The relative rates of the three reactions, addition, isomerization and exchange, are 1.00, 0.03 (Table I) and 0.3 (Tables II and III). It follows that most of the exchanged hexene is exchanged 1-hexene. The over-all reaction pattern is very similar to that observed on metallic catalysts in the vapor phase. In particular the isotopic distribution patterns of hexane resemble those observed in the deuterogenation of propylene on platinum-on-pumice at the lower temperatures and at the smaller ratios of deuterium to olefin[6] and those obtained in the deuterogenation of 1-hexene on nickel catalysts.[13] Thus, the mechanisms of these reactions appear to be substantially the same in the vapor phase and in hydrocarbon solution.

1-Hexene isomerizes initially to a nearly equilibrium mixture of *cis*- and *trans*-2-hexene (Table I). At 60% hydrogenation, no 3-hexenes could be detected although the estimated equilibrium composition of the vapor phase at 298° K. is[14]: 1-, *cis*-2-, *trans*-2-, *cis*-3- and *trans*-3-hexene, 1, 19, 47, 8 and 24%. The *cis*-2-/*trans*-2- ratio from these figures is 0.4 whereas our experiments give 0.6 at all conversions. The discrepancy probably lies within the over-all experimental uncertainty.

The 2-hexenes accumulate steadily throughout the hydrogenation and, near complete conversion, the residual hexenes are largely 2-hexenes (see particularly run 12c, Table I). Thus, selectivity for hydrogenation of 1-hexene is high; little 2-hexene is hydrogenated in its presence.

Selectivity for hydrogenating 1-hexene *vs.* 2-hexene, the rate of isomerization of 1-hexene, and the *cis*/*trans* ratio of the 2-hexenes were the same for hydrogen as for deuterium to within the rather poor precision in measuring 2-hexene.

The hexane product contains all species from hexane-$d_0$ to hexane-$d_{14}$ (Table III, runs 31b and 31c) but mainly hexane-$d_0$ to hexane-$d_6$. The average deuterium content is almost 2.00 at complete deuterogenation as shown by runs 14c and 31c in Table III but only about 1.7 at low conversions. The missing deuterium, 2.0–1.7, is stored in the exchanged hexenes. As these deuterogenate, the stored deuterium is recovered and the deuterium content of the hexane rises by decrease in the content in hexane-$d_0$ and increase in that in hexane-$d_3$ and hexane-$d_4$. At intermediate degrees of reaction, addition of the deuterium contents of hexane and hexene gives a proper balance. Thus, in the run in Table II which had proceeded to 43.1% deuterogenation, $0.431 \times 1.71 + 0.569 \times 0.17 = 0.851$ as against $2.00 \times 0.431 = 0.862$.

It follows that there is no isotopic exchange between gas phase deuterium and the hydrogen atoms of alkane or alkene, *i.e.*, the gas phase remains devoid of hydrogen. Had such exchange

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[13] R. L. Burwell, Jr., and R. H. Tuxworth, *J. Phys. Chem.*, **60**, 1043 (1956).

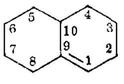
[14] F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie University Press, Pittsburgh, 1953, p. 738.

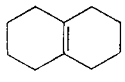
occurred, the final deuterium content of hexane would have exceeded 2.0.

The small ratio of the rate of isomerization to to that of hydrogenation seems characteristic of platinum catalysts[9,15] in contrast to a large ratio with palladium catalysts.[5a,16] The rate of isotopic exchange of olefin relative to that of deuterogenation seems to be larger for platinum than for nickel,[17] although strictly comparable data are unavailable.

**Deuterogenation of Octalins.**—No significant formation of isomeric octalins could be detected during hydrogenation of either $\Delta^{1,9}$- (XII) or $\Delta^{9,10}$-octalin (XIII). Because of the highly selective hydrogenation of XII (see section on Materials), it could not have isomerized to XIII since that then would have accumulated as did the 2-hexenes. However, XIII could have isomerized to XII, which then could have hydrogenated so rapidly as to escape detection.

XII





XIII

Isotopic exchange of both octalins accompanied their deuterogenations. Relative rates of these processes on the catalyst pre-reduced in acid are given in Table VI.

Table VI

Relative Rates of Deuterogenation, Isomerization and Exchange

| Olefin | Addition of deuterium | Isomerization of olefin | Exchange of olefin[b] |
|---|---|---|---|
| 1-Hexene | (1.00) | 0.03 | 0.30 |
| $\Delta^{1,9}$-Octalin | 0.8 | .00 | .08 |
| $\Delta^{9,10}$-Octalin | 0.03 | .00 (0.03[a]) | .006 |

[a] Relative rate of isomerization if hydrogenation proceeds through $\Delta^{1,9}$-Octalin. [b] Measured rate. Considering that the surface content in H is somewhat over 20%, gross rate is greater and particularly if an isotope effect should favor the introduction of hydrogen.

That $\Delta^{9,10}$-octalin is not hydrogenated on the catalyst reduced *in situ* but is on the catalyst pre-reduced in dilute acid is probably related to removal of the several per cent. of sodium which accompanies the catalyst made by the Adams method,[18] probably as the nitrite or nitrate.[19] Elimination of the sodium compounds previously has been reported to introduce changes in catalytic behavior.[18,19] In particular, benzene is not reduced on the ordinary catalyst unless an acid, for example acetic acid, is added. The washed catalyst requires the addition of no acid.[18]

According to current views, $\Delta^{1,9}$-octalin may absorb on either side of the plane of the double bond to form accordingly 1,9-diadsorbed *cis*-decalin or 1,9-diadsorbed *trans*-decalin.[9,15,20] On this picture, hydrogenation *via* each diadsorbed species is nearly equally probable since we obtained a *cis*/*trans* ratio in the decalins of 1.17 in run 30 and 1.08 in run 29 (Table IV, standard catalyst with added acetic acid).

The isotopic distribution patterns of the decalins resulting from the deuterogenation of $\Delta^{1,9}$-octalin (Table V) are of the same general type as those observed for hexane (Table II). Further, the total consumption of deuterium in deuterogenation and in olefin exchange amounts to 2.0 atoms per molecule of octalin hydrogenated. As with 1-hexene, no hydrogen is transferred to the gas phase deuterium. The decalins resulting from the deuterogenation of $\Delta^{9,10}$-octalin are much more extensively exchanged. In run 27, Table V, the average deuterium consumption was 2.98 atoms of deuterium per molecule of octalin deuterogenated. Hydrogen therefore was introduced into the gas phase deuterium, but the resulting isotopic dilution was very small because of the large ratio of deuterium to octalin which we employed.

**The Isotopic Distribution Patterns of the Decalins Derived from $\Delta^{1,9}$-Octalin.**—According to the conventional theory described in the introduction and in Fig. 1, the surface contains adsorbed deuterium and hydrogen atoms. Let the ratio be $a/b$. Two of these atoms must add to the olefin. Alternation between mono- and diadsorbed decalins will lead to the equilibration with the surface deuterium-hydrogen pool of hydrogen atoms at other positions.

Thus, the decalins consist of a series of species, decalin-$(h,d)_2$ in which two positions have been equilibrated, $-(h,d)_3$ with three, $-(h,d)_4$, *etc.* The fractions of each such species will be designated $N_2$, $N_3$, $N_4$ *etc.* Decalin-$(h,d)_n$ will appear as a random distribution of the possible deuteriated species, decalin-$d_0$, $-d_1$, $-d_2$ .... $-d_n$, where $d_m(n)$, the fraction of the species $-(h,d)_n$ which has gained $m$ deuterium atoms and $s$ hydrogen atoms ($m + s = n$), is

$$d_m(n) = \frac{(a/b)^m n!}{(1 + a/b)^n m! s!} \qquad (1)$$

The fraction of molecules with $m$ deuterium atoms $d_m$ in the total of each decalin is then[21]

$$d_m = \sum_i d_m(n) N_n, \; n > m \qquad (2)$$

The mass spectrometer gives its data in terms of the $d_m$'s but what one needs for consideration of mechanism is the $N_n$'s. Two approaches may be made. One may attempt to convert the $d_m$'s into $N_n$'s with the minimum introduction of mechanism as will be done in the next section, or one may attempt to fit the parameters of a particular model to derive $N_n$'s which then yield the observed $d_m$'s as will be done here.

In the model of Fig. 1, the values of the $N_n$'s will be determined by the ratios of the rates with which each monoadsorbed species desorbs or reverts to diadsorbed species. Consider a simplified model in which all mono- and diadsorbed species behave identically. The isotopic distri-

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[15] S. Siegel and G. V. Smith, *J. Am. Chem. Soc.*, **82**, 6082 (1960).

[16] S. Siegel and G. V. Smith, *ibid.*, **82**, 6087 (1960).

[17] J. N. Wilson, J. W. Otvos, D. P. Stevenson and C. D. Wagner, *Ind. Eng. Chem.*, **45**, 1480 (1953).

[18] C. W. Keenan, B. W. Giesemann and H. A. Smith, *J. Am. Chem. Soc.*, **76**, 229 (1954).

[19] M. C. Dart and H. B. Henbest, *J. Chem. Soc.*, 3563 (1960).

[20] For reviews of the background of this concept, see ref. 5a, p. 918 and ref. 5b.

[21] For the general background of this problem, see (a) G. Dallinga and G. ter Maten, *Rec. trav. chim.*, **79**, 737 (1960); (b) C. Kemball and I. Woodward, *Trans. Faraday Soc.*, **56**, 138 (1960).

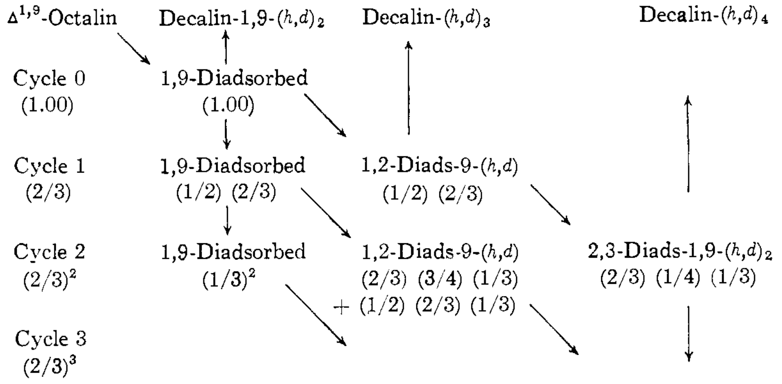

Fig. 2.—Hydrogenation–exchange process.

bution pattern then is determined by $k_1/(k_1 + k_2)$ in

$$\text{monoadsorbed decalin}\begin{cases}\xrightarrow{k_1}\text{desorbed decalin}\\ \xrightarrow[k_2]{}\text{diadsorbed decalin}\end{cases}\qquad(3)$$

Obviously $n$ in $-(h,d)_n$ cannot exceed 18. Further, the hydrogen atoms in *cis*-decalin are located in one set of 10 and two sets of 4 positions which cannot be connected by any vicinally diadsorbed species.[7] Thus, barring the intervention of some species such as XI (Introduction) the maximum value of both $m$ and $n$ in *cis*-decalin would be 10. *trans*-Decalin contains two sets of 9 hydrogen atoms at non-interconnecting positions.

Three regions for the quantity, $k_1/(k_1 + k_2)$ need consideration.

(a) If the quantity is very small all the values of $N_n$ approach zero except that of $N_{max}$, *i.e.*, all available hydrogen atoms are equilibrated with the surface deuterium/hydrogen pool. The particular details of the exchange process become irrelevant.

(b) If the quantity is 1.00, $N_2 = 1.00$ and the other $N_n$'s are zero. This corresponds to the sequence I, II, III, IV in Fig. 1.

(c) If the quantity has an intermediate value, and we shall take $^1/_3$ as the example, exchange proceeds as shown in Fig. 2 for adsorbed *trans*-decalin. On the assumption that all mono-and diadsorbed species behave identically, the content in 8,9-diadsorbed *trans*-decalin-1-$(h,d)$ has been included in that of the 1,2-diadsorbed-9-$(h,d)$. In each cycle, $^1/_3$ of the monoadsorbed molecules which form from the diadsorbed are desorbed, $^2/_3$ revert to diadsorbed molecules in the next cycle. The figures under the cycle number represent the fraction of the decalin originally adsorbed as *trans*-1,9-diadsorbed decalin which remains on the surface at each cycle. The other figures represent the fraction of the material on the surface at a particular cycle which constitutes the listed species. The value of $N_2$, then, is one-third of the sum of all the numbers under the decalin-$(h,d)_2$ column. The resulting values are: $N_2$, 0.50; $N_3$, 0.333; $N_4$, 0.1191; $N_5$, 0.0344; $N_6$, 0.0095.

Under the assumptions used in constructing Fig. 2, 9,10-diadsorbed *trans*-decalin is impossible, and the position of adsorption cannot shift from one side of the ring to the other (*i.e.*, the rate of formation of species XI or its equivalent is negligible).

Table VII presents computed isotopic distributions for the *trans*-decalin of run 30. In column B, $N_9 = 1.00$. This is case (a) above with half of the *trans*-decalin hydrogen atoms equilibrated with the deuterium–hydrogen pool. The random pattern for eighteen atoms, column C, differs little. Column B is unsatisfactory in three particulars. (1) The pattern is much too little peaked at $d_2$. (2) The pattern falls off too rapidly beyond $d_5$. (3) The value of $d_0$ is too large. For random exchange with $N$ large, $a/b$ must be rather small if $d_{av}$ is to equal 2.0. This will make the computed $d_0$ much too large.

For a rather similar isotopic distribution pattern obtained in deuterogenating *cis*-2-butene on nickel–silica at −78°, which deviated from a random pattern mainly in too much $d_2$, Wilson, Otvos, Stevenson and Wagner[17] suggested a composite process in which $N_2$ as well as $N_{max}$ was assumed non-zero, *i.e.*, case (a) plus case (b). The value of $a/b$ was assumed infinite for the process leading to $N_2$; for $N_{max}$ it then was chosen to give the observed $d_{av}$. This idea is applied in column D in Table VII but with $a/b$ for $N_2$ taken to give the over-all $d_{av}$. Objection (1) is removed but (2) and (3) remain. No such process can remove objection (3) nor can any process which makes $a/b$ smaller than about 2.0.

Column E represents case (c) and Fig. 2. It fits the data much better than columns B and C but is unsatisfactory principally in having $d_2$ too low and $d_3$ too high. The fit for $d_0$ through $d_4$ can be much improved by setting $k_1/(k_1 + k_2) = {}^1/_2$ rather than $^1/_3$ but contents in more exchanged species then fall off much too rapidly.

We think that the fit in column E is about as good as one can expect from any model which assumes that all sections of the catalyst surface are equivalent. In isotopic exchange between alkanes and deuterium, $k_1/(k_1 + k_2)$ must be assumed to have different values on different sections of the surface (perhaps on different crystal planes).[22,23] A simple case is presented in column F. Here, the product is assumed to result equally

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

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

from two types of surface, one with $k_1/(k_1 + k_2) = 1$ and one with it equal $^1/_3$. The value of $a/b$ is assumed the same on both sections. The fit is rather good although the concentrations of the highly exchanged species decline too rapidly.

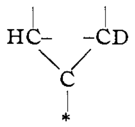
Table VII

Computed Distribution Patterns for *trans*-Decalin, Run 30, Table V

| | A<br>Obsd. | B<br>$N_9 = 1.0$ | C<br>$N_{18} = 1.0$ | D[a]<br>$N_2 = N_{18} = 0.5$ | E[b]<br>$(k_1/k_1 + k_2) = 0.333$ | F[c]<br>As E + $N_2 = 0.5$ |
|---|---|---|---|---|---|---|
| $a/b$ | | 0.254 | 0.114 | 0.114[a] | 2.06 | 3.45 |
| $d_0\%$ | 4.1 | 13.3 | 14.7 | 7.3 | 6.6 | 4.0 |
| $d_1$ | 26.9 | 29.7 | 29.7 | 23.8 | 30.4 | 28.4 |
| $d_2$ | 56.0 | 30.3 | 28.4 | 55.2 | 41.9 | 53.0 |
| $d_3$ | 9.5 | 18.0 | 17.0 | 8.5 | 16.4 | 10.7 |
| $d_4$ | 2.4 | 6.89 | 7.18 | 3.59 | 3.96 | 3.0 |
| $d_5$ | 0.68 | 1.76 | 2.26 | 1.13 | 0.81 | 0.70 |
| $d_6$ | .24 | 0.30 | 0.55 | 0.275 | 0.14 | 0.14 |
| $d_7$ | .08 | .033 | .106 | .050 | | |
| $d_8$ | .03 | .002 | .016 | .008 | | |
| $d_9$ | .01 | | .002 | .001 | | |

[a] $^1/_2$ model (a), $a/b = 0.114$; $^1/_2$ model (b), $a/b = 10.8$. [b] Model (c). [c] $^1/_2$ model (c) + $^1/_2$ model (b), $a/b = 3.45$ for both.

This treatment ignores isotope effects.[21b] In reverting to a diadsorbed species, the monoadsorbed species has been assumed to cleave a carbon–deuterium bond as easily as a carbon–hydrogen bond. If, as is likely, the latter bond cleaves more easily, the formation of the more highly exchanged species would be favored.



It appears probable, then, that case (c) can accommodate the results with a somewhat heavier weighting for decalin-$(h,d)_2$ although one cannot claim that the data rigorously establish this. It does, however, appear very likely that $N_2$ is about 0.75 as is the case in the model of column F, *i.e.*, most of the *trans*-decalin has been attached to the surface only at positions 1 and 9.

We have not attempted to explain one feature of the isotopic distribution patterns. That is, in any given run, the ratio $d_m/d_{m+1}$ is very nearly constant at $m = 4$ and beyond. In case (c) this requires $N_n/N_{n+1}$ also to be constant at $n = 4$ and beyond

$$N_n/N_{n+1} = (d_m/d_{m+1} + b/a)/(1 + b/a) \quad (4)$$

It is not clear just how such a very simple result would occur on a heterogeneous surface.

The *cis*-decalin of run 30, Table V, differs from the *trans* in the higher contents in $d_3$ to $d_{10}$. We suggest that this results from 9,10-diadsorbed *cis*-decalin which is permitted unlike its *trans* analog. The hydrogen atom at position 10 is, thus, immediately available for exchange in contrast to the situation with adsorbed *trans*-decalin.

**Deuterogenation of $\Delta^{9,10}$-Octalin.**—As with decalins from $\Delta^{1,9}$-octalin, those from $\Delta^{9,10}$-octalin exhibit a constant value of $d_m/d_{m+1}$ at larger values of $m$. In run 27, Table V, the ratio is constant at $d_5$ and beyond and equals about 2.0. However, the ratio $d_4/d_5$ is larger, whence $N_4/N_5$ is larger. Inspection of the *trans*-decalin from this run suggests that $N_2$ must be nearly zero. The calculated values of $N_2$ to $N_5$ in Table VIII were obtained by trial and error optimumization. The value of $a/b$ was chosen to give the best fit to $d_0$, $d_1$ and $d_2$. The fit for *trans*-decalin is rather good for $N_2 = 0$ but *cis*-decalin clearly requires a non-zero value for $N_2$. Slightly different values of the $N_n$'s result from other choices of $a/b$ but the possible range of variation is not large. We consider that $N_2$ can be said to lie between 0.00 and 0.05 for *trans*-decalin and between 0.13 and 0.20 for *cis*.

Table VIII

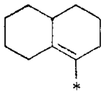
Computed Distribution Patterns for Decalins of Run 27

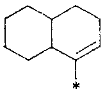
$a/b = 3.45$, $N_{n+1}/N_n = 0.563$ at $N_5$ and greater

| | *trans*-Decalin | | | *cis*-Decalin | | |
|---|---|---|---|---|---|---|
| | $N$ | $d$(calcd.) | $d$(obsd.) | $N$ | $d$(calcd.) | $d$(obsd.) |
| 0 | ... | 0.014 | 0.022 | ... | 0.013 | 0.029 |
| 1 | ... | .082 | .084 | ... | .113 | .100 |
| 2 | 0.000 | .300 | .286 | 0.155 | .314 | .311 |
| 3 | .624 | .406 | .405 | .415 | .323 | .323 |
| 4 | .227 | .122 | .122 | .252 | .139 | .139 |
| 5 | .065 | .041 | .042 | .078 | .049 | .049 |
| 6 | .036 | .0205 | .020 | .044 | .0245 | .024 |
| 7 | .0202 | .0103 | .010 | .0246 | .0123 | .012 |

The following explanation seems probable. All of the *trans*- and most of the *cis*-decalin derive from a common intermediate with one fewer hydrogen atoms than octalin. Only about 10% of the reactant forms decalin by hydrogenation of $\Delta^{9,10}$-octalin *via* initial formation of 9,10-diadsorbed *cis*-decalin, *i.e.*, that represented by $N_2$ for *cis*-decalin.

Correspondingly, no large portion of the *trans*-decalin can result from an intermediate in which four or more hydrogen atoms have been necessarily equilibrated since $N_3$ for *trans*-decalin is large. This excludes the appropriate species XI,[5a,8] XIV, as the intermediate since the hydrogen atom at position 10 would have been equilibrated during its formation. None the less, some species such as XIV or XV has some probability of occurrence since otherwise we would not observe species more exchanged than $d_{10}$ for *cis*-decalin nor $d_9$ for *trans*.


XIV


XV

As has been observed frequently, the rate of hydrogenation and particularly the selectivity for hydrogenation of an ethylene steadily decreases with increasing substitution. The contrast between $\Delta^{1,9}$- and $\Delta^{9,10}$-octalin is so marked as to lead to a change in mechanism. However, 9,10-diadsorbed *cis*-decalin does not seem unstable *per se*, since as mentioned above this species seems to be formed from other diadsorbed *cis*-decalins. Further, 2,3-diadsorbed 2,3-dimethylbutane seems to form readily.[6] The slow rate of conversion of tetrasubstituted olefins to the corresponding diadsorbed molecules may be a matter of steric hindrance.

Two possible common intermediates are: (a) $\Delta^{1,9}$-octalin-10-(*h,d*) formed by preliminary isomerization and (b) some symmetric adsorbed species (decalin minus three hydrogen atoms).[7,13,21] Siegel and Smith[15] have studied the hydrogenation of a similar olefin, 1,2-dimethylcyclohexene, on platinum in acetic acid solution. They have proposed a mechanism involving an isomerization as in (a). However, they propose that the isomerization occurs *via* the classical mechanism of Fig. 1. We doubt that that is true in the present circumstances. It would involve the preliminary formation of 9,10-diadsorbed *cis*-decalin which then proceeds *via* 9-monoadsorbed to 1,9-diadsorbed decalin which desorbs as $\Delta^{1,9}$-octalin-10-(*h,d*). In view of the rapid adsorption and conversion of $\Delta^{1,9}$-octalin without isomerization to $\Delta^{9,10}$-octalin this seems improbable.

The greater yield of *cis*-decalin from the hydrogenation of $\Delta^{1,9}$-octalin than from that of $\Delta^{9,10}$ octalin is consistent with possibility (a) since decalin-$(h,d)_2$ could only be *cis*. We hesitate to place much weight upon such an argument because, although the hydrogenations of both octalins would proceed very largely *via* hydrogenation of $\Delta^{1,9}$-octalin, the conditions would be quite different: tiny concentrations of $\Delta^{1,9}$- in the presence of much $\Delta^{9,10}$-octalin in one case, large concentrations of $\Delta^{1,9}$-octalin, in the other. Consequently, the *cis/trans* ratio of product decalin need not be identical in the two cases.

**The Average Deuterium Content.**—Why is the average deuterium content 2.0 in deuterogenation of 1-hexene and $\Delta^{1,9}$-octalin but much larger in that of $\Delta^{9,10}$-octalin? The value of $d_{av}$ can exceed 2.0 only as the rate of exchange between adsorbed hydrogen atoms and gas phase deuterium becomes significant with respect to the rate of deuterogenation. Thus, if the rate of exchange is constant, the faster the deuterogenation, the less $d_{av}$ will exceed 2.0. Two additional factors which may affect $d_{av}$ should be noted. (a) In the more rapid hydrogenations, the surface coverage by H(D)-atoms will be lower and the rate of desorption of hydrogen deuteride will be less. (b) Serious concentration gradients of hydrogen may exist in the catalyst pores. In the liquid phase, the concentration of olefin is many orders of magnitude greater than that of hydrogen. Thus, although olefin concentration gradients may well be larger than those of hydrogen, the fractional change in olefin concentration between the bulk liquid phase and the catalyst interstices is negligible. Contrariwise, the equilibrium hydrogen concentration in the liquid phase is so small that even a small concentration gradient could bring the hydrogen concentration to zero before the center of the catalyst particle was reached. Thus, hydrogen deuteride may desorb into the pores in both cases but have a substantial relative rate of escape only with the slowly hydrogenating $\Delta^{9,10}$-octalin. Rate limiting diffusion of hydrogen in the pores has been indicated for similar hydrogenations on nickel–kieselguhr.[7]

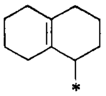
What would be the effect of replacing the hydrocarbon solvent by one of the type ROD? It is known that exchange between gas phase deuterium and the hydroxylic hydrogen atom in acetic acid is fast relative to hydrogenation on platinum catalysts.[24] This is probably true for ethanol. In deuterogenating an olefin with deuterium and $CH_3COOD$, $CH_3COOH$ can serve as a transport agent for hydrogen from the inside of a catalyst particle to its surface where $CH_3COOH$ can exchange hydrogen with liquid phase deuterium. Further, the quantity of available deuterium in the catalyst pores would be much larger when $CH_3COOD$ is used as solvent and correspondingly, the surface fraction of deuterium or $a/b$ would be much larger. Thus, one would expect to find $d_{av}$ much larger. Such deuterogenation of certain steroids does seem to yield a $d_{av}$ distinctly larger than 2.0.[25,26] A deuterogenation of methyl oleate on platinum[27] is also of this type. Isotopic exchange was very extensive and $d_{av}$ was much larger than 2.0.

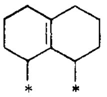
Two deuterogenations in ethanol solution also are probably similar, although exchange with solvent ethanol may have complicated the issue since ethanol-$d_0$ was employed.[28,29]

**Olefin Exchange and Isomerization.**—The classical mechanism for the exchange of $\Delta^{9,10}$-octalin would necessitate the conversion of 9,10-diadsorbed decalin to 1,9-diadsorbed followed by reconversion to 9,10-diadsorbed and desorption. This would yield $\Delta^{9,10}$-octalin-1-*d*. However, 1,9-diadsorbed decalin formed initially during the hydrogenation of $\Delta^{1,9}$-octalin does not lead to the formation of $\Delta^{9,10}$-octalin. Thus, the classical method is not operative here.

As is well known, alkanes exchange with deuterium on metallic catalyst under conditions more drastic than those required for hydrogenation.[4,5] Decalins will not exchange under the conditions of the present experiments. However, the carbon–hydrogen bond dissociation energy at allylic positions is about 15 kcal. weaker than that in the equivalent decalin, and its rate of dissociative adsorption would be considerably augmented on almost any picture of the transition state. A similar process at position-2 should proceed little if any faster than in decalin itself. Thus, we conclude that 1-monoadsorbed $\Delta^{9,10}$-octalin (XVI) is the intermediate principally responsible for exchange.

XVI





XVII

As shown by experiment 27, Table V, the deuterium distribution in exchanged octalin is far from random. Reaction of the monoadsorbed octalin, XVI, to a diadsorbed octalin, XVII, would be favored by the same considerations which favored initial formation of the monoadsorbed octalin.

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[24] M. L. Eidinoff, J. E. Knoll, D. K. Fukushima and T. F. Gallagher, *J. Am. Chem. Soc.*, **74**, 5280 (1952).

[25] D. K. Fukushima and T. F. Gallagher, *ibid.*, **77**, 139 (1955).

[26] E. J. Corey, G. A. Gregoriou and D. H. Peterson, *ibid.*, **80**, 2338 (1958).

[27] N. Dinh-Nguyen and R. Ryhage, *Acta Chim. Scand.*, **13**, 1032 (1959); *J. Research Inst. Catalysis, Hokkaido University*.

[28] E. L. Eliel, P. H. Wilken and F. T. Fang, *J. Org. Chem.*, **22**, 231 (1957).

[29] W. A. Bonner and J. B. McKay, *J. Am. Chem. Soc.*, **82**, 5350 (1960).

Such a species could account for much of the departure from a random isotopic distribution.

The simplest classical sequence, $\Delta^{1,9}$-octalin$\rightarrow$ 1,9-diadsorbed decalin$\rightarrow$9-monoadsorbed$\rightarrow$1,9-diadsorbed$\rightarrow$$\Delta^{1,9}$-octalin, cannot form $\Delta^{1,9}$-octalin-1-*d*, since the deuterium atom added at position 1 in the second step would of necessity be removed in the third unlike the situation obtaining in acyclic compounds in which rotation about carbon–carbon single bonds is possible.[30]

A classical sequence involving a double bond shift could form $\Delta^{8,9}$-octalin-1-*d*. However, it is hard to see why the formation of $\Delta^{9,10}$-octalin should not accompany this since 9-monoadsorbed *cis*-decalin would be one intermediate. In general, our evidence suggests that the rate of desorption of $\alpha,\beta$-diadsorbed decalins is very slow under our conditions. Further, in the classical mechanism the formation of exchanged olefin and of product have most of the steps in common. One would expect some resemblance between the isotopic distribution patterns of octalin and decalin. Yet, in experiment 30, the patterns contrast markedly: little but single exchange of octalin, multiple exchange beyond $d_2$ in decalin.[31]

Our evidence does not distinguish among the remaining possibilities: (a) Dissociative adsorption at an allylic position to form 2- or 8-monoadsorbed $\Delta^{1,9}$-octalin. In this case, models indicate that the further formation of 2,8-diadsorbed octalin would not be favored. (b) Dissociative adsorption to form 1-monoadsorbed $\Delta^{1,9}$-octalin (XIV). (c) A concerted process forming $\Delta^{8,9}$-octalin-1-*d*.[32] These processes would be independent of that leading to hydrogenation. Determination of the position of deuterium introduction would be helpful in distinguishing among the possible mechanisms.

Similar considerations apply to the isotopically exchanged hexenes, but the situation is complicated by olefin isomerization which also should introduce deuterium. The heavily predominant formation of isotopically exchanged 1-hexene rather than that of the far more stable 2-hexene suggests that some process other than that of Fig. 1 may be involved, but not primarily a process such as (c) above which would of necessity lead to a double bond shift.

**Conclusions.**—With the possible exception of the appearance of serious concentration gradients of dissolved hydrogen in the catalyst pores, our results for liquid phase hydrogenation closely resemble those in the vapor phase. It appears very unlikely that there is any substantial difference between the mechanism of hydrogenation on platinum catalysts in the vapor phase and that in the liquid phase.

In hydrogenating mixtures of olefins, the less substituted ethylene hydrogenates with very high selectivity.

Relative to hydrogenation, the isomerization of olefins on platinum oxide is either slow (1-hexene and possibly $\Delta^{9,10}$-octalin) or negligible ($\Delta^{1,9}$-octalin). However, the rate of production of exchanged but unisomerized olefin is relatively large and amounts to about $^1/_6$th that of the rate of hydrogenation.

The isotopic distribution patterns of the product alkane can be analyzed into a series of species, alkane-$(h,d)_2$, alkane-$(h,d)_3$, . . . where $n$ in alkane-$(h,d)_n$ represents the number of hydrogen atoms which have been equilibrated with the surface hydrogen/deuterium pool. For 1-hexene and $\Delta^{1,9}$-octalin, the fraction of material with $n = 2$ is about 60–75%. The fraction falls off rapidly with increasing $n$. The data seem consistent with preliminary adsorption of the olefin as a *vic*-diadsorbed alkane, conversion to mono-adsorbed alkane followed by alternation between mono- and diadsorbed alkane. The rate of reversion of mono- to diadsorbed alkane is 2 to 3 times that of conversion of mono-adsorbed alkane to desorbed alkane.

$\Delta^{9,10}$-Octalin is deuterogenated at a negligible rate upon ordinarily reduced platinum oxide. It is necessary to add acetic acid or to pre-reduce the platinum oxide in dilute acid followed by protracted evacuation to get reasonable rates, although even on the pre-reduced catalyst $\Delta^{1,9}$-octalin is hydrogenated nearly 30 times as rapidly as $\Delta^{9,10}$-octalin. The product is about 61% *cis*-decalin (39% *trans*-decalin) for the latter octalin as compared with 54% *cis* for the former.

The fraction of -$(h,d)_2$ is 0.0 for the *trans*-decalin produced from $\Delta^{9,10}$-octalin and the fraction for the *cis* is 0.15. Thus, about 90% of the total product appears to proceed through a common intermediate which has one fewer hydrogen atom than octalin. The intermediate must be capable of conversion to either *cis*- or *trans*-decalin. Such an intermediate could be $\Delta^{1,9}$-octalin-10-*d* formed by preliminary isomerization of $\Delta^{9,10}$-octalin. The isomerization must proceed by a mechanism independent of that involved in hydrogenation.

The value of $d_{av}$ is 2.0 in the deuterogenation of 1-hexene and $\Delta^{1,9}$-octalin but considerably larger in that of $\Delta^{9,10}$-octalin. Exchange between adsorbed hydrogen atoms and gas phase deuterium appears to be a relatively slow process. It becomes significant only for the much slower deuterogenation of the last olefin.

There is rather strong evidence that isotopic exchange of $\Delta^{9,10}$-octalin proceeds *via* 1-monoadsorbed $\Delta^{9,10}$-octalin. Whether such an allylically adsorbed species is important in other olefin exchange processes has not been established.

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[30] For example, ref. 26 reports that *hydrogenation* of a $\Delta^{9,11}$-pregnane-11-*d* puts the 11-*d* into a set which is non-interacting with those positions into which the 9,11-diadsorbed pregnane can transform. In our case, the hydrogen atom at C-1 cannot interact with the surface.

[31] See also ref. 17 for a similar situation for exchanged butene on nickel–kieselguhr catalysts in gas phase deuterogenation.

[32] J. Turkevich and R. K. Smith, *J. Chem. Phys.*, **16**, 466 (1948).