

greatly influence the basicity of silanol oxygen,^{7,8} must be modified accordingly.

Our data also indicate that pi-bonding is much stronger in Ph₃SiOH than in Ph₃GeOH. On the basis of inductive effects alone, Ph₃GeOH would be expected to be a stronger acid and a weaker base than Ph₃SiOH, while in fact the reverse is true. The high basicity of Ph₃GeOH can be attributed to the inductive effect of the germanium atom, which becomes apparent with weaker pi bonding in this compound.

Weak dative pi-bonding from oxygen to germanium probably does take place in Ph₃GeOH. The acidity of PhGeOH is approximately as great as that of Ph₃COH, while on the basis of inductive effects alone it should be much less. However, the data for Ph₃SnOH and Ph₃PbOH provide no indication of significant pi-bonding in these compounds.

Our conclusion is that in this series of compounds pi-bonding from oxygen to metal decreases markedly going from Si to Ge to Sn (and Pb).²³ This is in contrast to the theoretical predictions of Craig,^{5b} as well as to the findings of Chatt and Williams⁴ and of Benkeser,^{5a} that the pi-bonding from aromatic rings to these metals takes place to about

(23) Cf. R. West and R. H. Baney, *J. Phys. Chem.*, **64**, 822 (1960).

the same extent. Of course, dative pi-bonding from aromatic rings need not follow the same trend as pi-bonding from oxygen. The pi-electron cloud in the aromatic ring is perhaps more diffuse than the *p*-electron pairs on oxygen and hence may overlap better with the correspondingly diffuse *d* orbitals on the larger metal atoms.

Since our compounds were triphenyl derivatives, any dative pi-bonding from the aromatic rings which took place would compete with pi-bonding from oxygen. However, aromatic ring pi-bonding appears to be unimportant, in this series of compounds, compared to oxygen pi-bonding. Previously we have shown that trimethyl- and triethylsilanol are weaker acids and stronger bases than triphenylsilanol.⁷ Hence the net effect of the aromatic rings is electron-withdrawing; the opposite would be true if aromatic ring pi-bonding were important. Similarly, the chemical evidence suggests that trialkyltin hydroxides are more basic and less acidic than triphenyltin hydroxide.²⁴ The question of competitive pi-bonding between oxygen and aromatic rings will be considered in more detail in another publication.

(24) J. G. A. Luitjen and G. J. M. Van der Kerk, "Investigations in the Field of Organotin Chemistry," Tin Research Institute, Middlesex, England, 1955.

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

Reactions between Hydrocarbons and Deuterium on Chromium Oxide Gel. I. General¹

BY ROBERT L. BURWELL, JR.,² A. B. LITTLEWOOD, M. CARDEW, G. PASS AND C. T. H. STODDART

RECEIVED FEBRUARY 15, 1960

Sites for hydrogenation of olefins and for isotopic exchange between alkanes and deuterium are simultaneously developed by heating chromium oxide gel to higher temperatures. Above 470°, the rate of loss of surface exceeds the rate of site production. There is little interaction among sites. Chromium oxide gel also catalyzes double bond migration but on sites which, at least in part, differ from those involved in hydrogenation and exchange. The major processes, simple isotopic exchange of one atom per adsorption step and simple *cis*-addition of deuterium atoms to the double bond, involve a mono-adsorbed alkane which cannot revert to a diadsorbed alkane at temperatures below 300°. It seems probable that olefin reacts with a surface hydrogen atom to form monoadsorbed alkane without proceeding through diadsorbed alkane. The preference for exchange of primary hydrogen atoms and the relative rates of exchange of a series of hydrocarbons suggest that the transition state separating alkane and monoadsorbed alkane involves some small contribution from carbanion. The very rapid exchange of cyclopropane probably results not only from this but also from isovalent hyperconjugation with surface sites in which a *d-p* π -bond is involved. The minor processes, multiple deuteration in isotopic exchange and the spreading of isotopic distribution patterns in the addition of deuterium to olefin, cannot, in general, involve gas phase olefin as an intermediate. Because of the absence of the minor processes in ethane exchange and in the deuteration of ethylene, it seems probable that an adsorbed allylic species is the intermediate.

During recent decades, it has become possible to analyze the mechanisms of a large number of organic reactions in terms of a reasonably restricted group of elementary reactions. Tentative approaches to a similar development are evident in heterogeneous catalysis and particularly in reactions between hydrocarbons and hydrogen on metallic catalysts. However, since characterization of elementary reactions between hydrocarbons and hydrogen solely on the basis of experiments on

metallic catalysts might be seriously misleading, it seemed desirable to secure appropriate information on quite different catalysts. Accordingly, we have investigated a series of reactions on chromium oxide gel, chosen from the various catalysts of the oxide type because of its stability and because of the considerable information which has been accumulated about its catalytic and physical properties.

Paper I of this series will discuss our results and consider their mechanistic implications. Papers II-V will report the details of the isotopic exchange experiments, of the addition of deuterium to olefins and of the stereochemistry of these reactions.

The original work of Lazier and Vaughen³

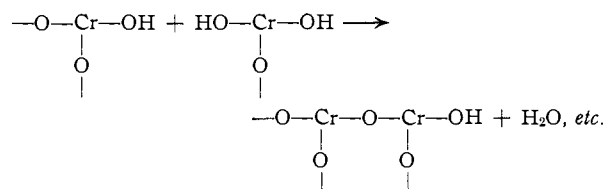
(1) Some of the material has been the subject of a preliminary communication, R. L. Burwell, Jr., and A. B. Littlewood, *THIS JOURNAL*, **78**, 4170 (1956), and also, Miami Meeting, American Chemical Society, April, 1957. General surveys have been presented at the Gordon Research Conference on Catalysis, 1959, and at the Conference on Organic Catalysis, Moscow, November 16, 1959.

(2) To whom inquiries concerning these papers should be directed.

(3) W. A. Lazier and J. V. Vaughen, *THIS JOURNAL*, **64**, 3080 (1932).

which has been confirmed by many workers indicates that good chromia catalysts are prepared by the slow addition of ammonium hydroxide with good stirring to a dilute solution of chromic nitrate. A very similar catalyst can be prepared much more readily by simmering a solution of urea and chromic nitrate.^{4,5} The hydrolysis of urea liberates ammonia slowly and with maximum uniformity. In both preparations, little visible change precedes abrupt and complete precipitation of a hydrous gel which is more than 99 vol. % water. It is generally agreed that the existence of such dilute gels implies that the gelling agent is present in fibrillar form and that the gel itself has a "brush heap" structure.⁶

The fibrils in chromium oxide gel can be represented as a condensation polymer of chromium hydroxide. Ignoring coordinatively bound water,



The exact structure of the fibrils is unknown although Selwood has proposed one possibility.⁷ It is not clear whether one should regard the gel as a micromolecular or a macromolecular gel.⁶ The latter classification is compatible with the usual all or none solubility of high polymers,^{8,9} and with the resolubilization of a freshly precipitated gel by a small addition of chromium nitrate.

Most of the water readily evaporates from the dark-green hydrous gel leaving a black material which is amorphous to X-rays and in which each chromium atom has fewer nearest neighbors than in crystalline α -chromia.⁷ The accompanying compaction of the structure and cross-linking of the fibrils is far from complete since the material has a surface area of several hundred square meters per gram. Per mole of Cr_2O_3 , the gel contains about 3.5 moles of water when dried at 120° and 0.5 mole when dried at 300°. Even at 450°, substantial quantities of water remain¹⁰ presumably as surface hydroxyl groups.

If the gel is heated too rapidly during its initial treatment, it may, as is well known, undergo a strongly exothermic crystallization to bright-green, macrocrystalline α -chromia. This occurs somewhere in the temperature range 275–375°. Once safely carried to above 400°, the gel is surprisingly stable and it even remains black following treatment at 550°. Apparently, a structure is developed by higher temperature treatment which is much

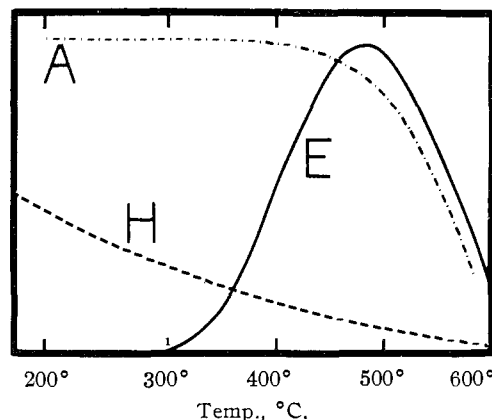


Fig. 1.—Schematic representation of activation of chromium oxide gel: A, surface area; H, % water; E, activity in catalyzing the exchange reaction between hexane and deuterium.

more resistant to transformation than is the initial gel as dried at 175°. Nevertheless, protracted use accompanied by numerous regenerations at 475° leads to the formation of microcrystalline α -chromia which, although black and indistinguishable visibly from the starting material, becomes a dark olive-green upon grinding (paper III, Techniques). Unaltered material would have remained black. Little of the present work was devoted to study of this transformation but it is apparent that the catalytic properties of the amorphous and of the microcrystalline α -chromia are similar.

One of our samples had a surface area of 301 square meters per gram following initial heating to 320°; after subsequent heating to 470° the value was 278. As ample which had been heated to 570° and used for some catalytic runs, and which showed declining activity, had a surface area of 62. The BET method with nitrogen was employed for the measurement of surface area. X-Ray examination of the last catalyst showed that it was α -chromia.

A. Activation.—Chromium oxide gel acquires significant activity as a catalyst for isotopic exchange between alkanes and deuterium or for hydrogenation of olefins only after activation by exposure to higher temperatures. This may be demonstrated by passing test mixtures of deuterium and hexane (mole ratio = 2) or of hydrogen and 1-hexene (mole ratio = 2) over a gel which has been dried at 175°. The catalyst temperature is slowly increased.

With the first mixture, exchange is first observed at 300°. Catalytic activity reaches a maximum at about 470° and then declines. This is shown schematically in Fig. 1 along with accompanying changes in surface area and water content. For temperatures below 300°, the activity curve represents the degree of isotopic exchange as measured at the given temperature. Above 300°, the catalyst is treated in a stream of nitrogen at the indicated temperature but isotopic exchange is measured at 300°. The activation energy for this reaction is independent of the pretreatment temperature, 16 kcal. per mole (paper II, Table III).

(4) R. L. Burwell, Jr., and H. S. Taylor, *THIS JOURNAL*, **58**, 697 (1936).

(5) R. L. Burwell, Jr., *ibid.*, **59**, 1609 (1937).

(6) P. H. Hermans in "Colloid Science," Vol. II, edited by H. R. Kruyt, Elsevier Publishing Company, Amsterdam, 1949, Chapter XII.

(7) P. W. Selwood, M. Ellis and C. F. Davis, Jr., *THIS JOURNAL*, **72**, 3549 (1950).

(8) J. J. Hermans in "Colloid Science," Vol. II, edited by H. R. Kruyt, Elsevier Publishing Company, Amsterdam, 1949, p. 77f.

(9) A. E. Alexander and P. Johnson, "Colloid Science," Vol. II, Clarendon Press, Oxford, 1949, pp. 786–796.

(10) D. J. Salley, H. Fehrer and H. S. Taylor, *THIS JOURNAL*, **63**, 1131 (1941).

With our flow rates, isotopic exchange on the most active catalysts can be measured at 200°.

With the hexene-hydrogen test mixture, hydrogenation first appears at 225°. Treatment of the catalyst at progressively higher temperatures leads to an increase in activity for hydrogenation which closely parallels that for isotopic exchange. An optimally activated catalyst causes complete hydrogenation of ethylene at -78°.

Double-bond migration accompanies hexene hydrogenation. This is first observed at about 175°. With activation, the rate of isomerization increases (compare runs T and U, Table II, paper IV) and isomerization becomes readily measurable at 125° (run W). However, the rate of increase of the rate of hydrogenation with activation much exceeds that of isomerization. Gas phase hydrogen is not required for isomerization since, at 200°, 1-hexene in a nitrogen stream is rapidly isomerized on an activated catalyst.

Similar reactions have been reported before on more or less similar catalysts but the feature of activation has not been appreciated. Heptane has been reported to exchange with deuterium at 330° and above on a Cr₂O₃-K₂O-Al₂O₃ catalyst.¹¹ Lazier and Vaughen⁸ reported that olefins could be hydrogenated but only at temperatures of 350°.¹² This high temperature requirement probably resulted from the presence of water vapor which is strong temporary poison.^{13,14} Weller and Voltz, however, have reported hydrogenation of ethylene at -78° on a sample of chromium oxide gel which had been cycled between hydrogen and oxygen treatments at 500° provided that it had been evacuated following the hydrogen treatment. The oxidized catalyst was inactive.¹⁵ Their pretreatment had converted the catalyst to crystalline α -chromia of about 35 square meters per gram. Isomerization of olefins at temperatures of 200-250° is well known.^{16,17}

Two types of activated adsorption of hydrogen on chromium oxide gel have been characterized⁴: one occurs with reasonable rapidity at about 200° and involves an activation energy of 22 kcal. per mole and the other at about 0° with a much lower activation energy. Ethylene exhibits activated adsorption detectable at 80° and above.¹⁸ In both cases the gels had undergone evacuation at 400° and should have been relatively active. However, the measured rates of adsorption are much too low to account for observed catalytic activity. Similarly, activated adsorption of ethane at 300° can hardly be detected manometrically,¹⁸ yet the adsorbent would, presumably, have given substantial rates of isotopic exchange. The hydrogen-

deuterium exchange reaction occurs on these catalysts at detectable rates at -190°¹⁹ yet no adequate rate of activated adsorption of hydrogen could be identified. It would, therefore, appear that the active sites for hydrogenation and exchange occupy but a very small fraction of the surface. The nature of the activation process supports this. At low levels of activation, the sites must be sparsely distributed. Yet, as will appear, the catalytic characteristics of the most and of the least activated catalysts seem to differ, not in nature, but only in total activity. In particular, as has been mentioned, the activation energies for isotopic exchange are the same for all degrees of catalyst activation.

Thus, the activation process generates sites for hydrogenation and isotopic exchange. These are relatively far apart and presumably non-interacting. The number of sites increases with increasing temperature of activation but, as shown in Fig. 1, beyond about 470°, sintering destroys surface faster than sites are generated and total activity declines.

In these papers, the catalysts were optimally activated unless otherwise stated. As necessary, catalysts were reactivated by a short treatment with nitrogen at 470-480°. Catalytic activities resulting from this treatment varied within a factor of about two. Loss in activity in isotopic exchange runs was small and reversible on activation. One catalyst was used for such runs over a period of eighteen months and subjected to many reactivations. Its catalytic characteristics at the end of the period were little changed from the initial. Catalysts were more apt to become unregenerable during olefin hydrogenation. However, one catalyst was used for over twenty deuteriogenations of simple olefins before its activity after reactivation began to fall. Deuterium plus 2-butyne or 2-pentyne killed the catalyst rapidly (paper IV) presumably by polymerization of the acetylene on the surface of the catalyst.

B. Isotopic Exchange of Alkanes.—The isotopic distribution patterns of exchanged alkanes represents a superposition of two separate exchange processes, simple exchange and extensive multiple exchange. Simple exchange, characterized by a random distribution of deuterium in the alkane molecules, occurred in all cases, and it was the only exchange process with methane, ethane, cyclopropane and 3,3-dimethylpentane. With the twelve other hydrocarbons investigated, it was accompanied by small amounts of extensive multiple exchange, characterized by the presence of highly exchanged species the concentrations of which would be zero on the random exchange model. Tables III and IV of paper III present examples of the analysis of isotopic distribution patterns into the two types of exchange (see also paper V, section C).

In a flow reactor, simple exchange characterizes a process in which one and only one deuterium atom is exchanged in each adsorption step (paper II, section A). At low conversions, monodeuteroalkane is nearly the exclusive product. At higher

(11) M. Ya. Kagan, L. A. Erivanskaya and I. V. Trofimova, *Doklady Akad. Nauk, S.S.S.R.*, **82**, 913 (1952).

(12) See also F. E. Frey and W. F. Huppke, *Ind. Eng. Chem.*, **25**, 54 (1933).

(13) H. S. Taylor and J. Turkevich, *Trans. Faraday Soc.*, **35**, 921 (1939).

(14) J. F. Woodman and H. S. Taylor, *THIS JOURNAL*, **62**, 1393 (1940).

(15) S. W. Weller and S. E. Voltz, *ibid.*, **76**, 4695 (1954).

(16) R. Ya. Levina and N. A. Shcheglova, *J. Gen. Chem. U.S.S.R.*, **11**, 527 (1941); R. Ya. Levina, N. M. Mezentsova and D. A. Akishin, *Zhur. Obshchei Khim.*, **23**, 562 (1953).

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

(18) J. Howard and H. S. Taylor, *THIS JOURNAL*, **56**, 2259 (1934).

(19) A. J. Gould, W. Bleakney and H. S. Taylor, *J. Chem. Phys.*, **2**, 362 (1934).

conversions, alkane- d_2 results from a second adsorption, then alkane- d_3 , and so on. The activation energy for simple exchange is about 16 kcal. for hexane, 15 for propane, 15 for *neopentane*, 22 for ethane and 7 for cyclopropane (paper II, section A, Table III, section B; III, sections A and B).

Relative rates of simple exchange of *molecules* of various alkanes and cycloalkanes are given in Table I. Values were determined by sandwich runs employing cyclohexane as the standard (see paper III, section D). Relative rates of exchange of *hydrogen atoms* are given in parentheses (this correction for the number of hydrogen atoms per molecule is treated at the end of paper III, section D. These values are somewhat arbitrary for molecules with more than one kind of hydrogen atom).

TABLE I
RATES OF EXCHANGE OF HYDROCARBONS RELATIVE TO
CYCLOHEXANE^a

Hydrocarbon	Relative rate	
	200°	235°
Cyclopropane	50 (100)	
Ethylcyclobutane	5.3 (7.1)	4.8 (6.4)
Cyclopentane	0.86 (1.0)	0.98 (1.2)
Cyclohexane	1.00 (1.00)	1.00 (1.00)
Methylcyclohexane	2.1	2.0
Cycloheptane	2.7 (2.3)	
Cyclooctane	5.4 (4.1)	
Methane		0.32 (0.96)
Ethane	0.13 (0.25)	0.18 (0.36)
Hexane	2.9 (3.9)	2.6 (3.5)
2,3-Dimethylbutane	1.3 (1.3)	1.2 (1.2)

^a Feed composition: deuterium/hydrocarbon = 2.0 except for cycloheptane and cyclooctane = 14.

The question now arises as to whether primary or secondary hydrogen atoms exchange more readily. The mass spectrographic fragmentation patterns of exchanged hexanes suggest that primary hydrogen atoms exchange about five times as readily as secondary. However, isotope effects upon fragmentation probabilities subject this figure to the possibility of a large error (paper II, section C). Accordingly, we examined exchanged propane for propane-1- d and propane-2- d by infrared spectroscopy. None of the latter species could be detected from which we conclude that, in propane, a primary hydrogen atom exchanges at least six times as fast as a secondary (paper II, section C). The somewhat more rapid exchange of *neopentane* than propane (paper II, Table V) confirms this conclusion.

However, secondary hydrogen atoms, at least those in cycloalkanes, do exchange. Further, as shown in Table I, the rate of exchange of hexane is only about three times faster than that of cyclohexane or cyclopentane. Thus, the relative rates of exchange of primary and secondary hydrogen atoms in propane might be somewhat atypical.

One may compute the relative rates of exchange of the methyl and of the ring hydrogen atoms in methylcyclohexane from the % D_0 determined from the parent peaks and from the cyclohexyl carbonium ion peaks. At 175, 200 and 230°, the relative reactivity of methyl and ring hydrogen atoms is 2.6. This figure is subject to error from

an isotope effect similar to but probably smaller than that discussed for hexane.

We conclude, then, that primary hydrogen atoms exchange somewhat but not enormously faster than secondary hydrogen atoms.

With hexane, the ratio of extensive multiple to simple exchange increases with increasing temperature. We are not sure as to the sign of the temperature coefficient of this ratio in the case of cyclohexane because the ratio varied by a factor of 2.5 from one reactivation to another. However, it seems clear that the temperature coefficient is larger for hexane than for cyclohexane.

Detailed examination of the isotopic distribution patterns of runs with cycloalkanes in Table III, paper III, shows that the quantities of cycloalkane- d_2 and - d_3 are too large by a few % of cycloalkane- d_1 (paper III, section C). The relative excess also varied from regeneration to regeneration but the variability did not correlate with that in extensive multiple exchange. Such excess D_2 and D_3 was much smaller or zero with alkanes (paper III, section C, Table IV).

Thus, at temperatures of about 200°, we observe a major process leading to simple exchange, a minor process leading, with cyclopentane-cyclooctane, to small excess amounts of D_2 and D_3 and a minor process leading to extensive multiple exchange for alkanes and cycloalkanes possessing chains of at least three carbon atoms in sequence none of which is quaternary (*i.e.*, 2,3-dimethylbutane and cyclopentane but not ethane nor 3,3-dimethylpentane).

C. Ring Cleavage.—The hydrogenolysis of the cyclopropane ring (paper III, section A) has an activation energy of 12 kcal., 5 kcal. greater than exchange. It becomes detectable relative to exchange at 75–100°. The cyclobutane ring undergoes hydrogenolysis at 200–235° but at a rate very small with respect to exchange (paper III, section C). No hydrogenolytic reactions were observed with any other hydrocarbons.

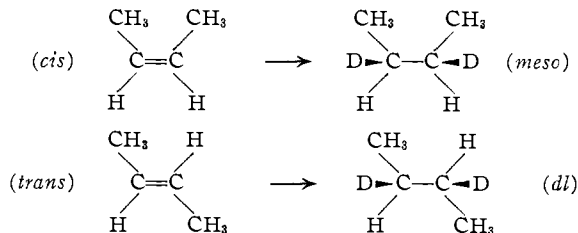
D. The Addition of Deuterium or Hydrogen to Olefins.—The isotopic distribution patterns of the products of the addition of deuterium to olefins on chromia catalysts at room temperatures are unusually simple. Unlike metallic catalysts, chromium oxide gel leads predominantly to the simple addition of two deuterium atoms to the double bond (paper IV, sections A and B).

At 0° and -78°, ethylene forms ethane-1,2- d_2 devoid of ethane- d_3 . Higher olefins give small amounts of alkanes more deuterated than the dideuterio. Propylene at -11° gives 1.5% propane- d_3 (paper IV, section A), and cyclopentene gives about the same result at 40° (paper IV, Table I). At such temperatures, 1-butene and 1-hexene give somewhat larger amounts of trideuterioalkane. 2-Butenes seem to give isotopically somewhat less pure products than 1-butene (paper V, Table I *vs.* paper IV, Table I). 2-Pentene gives the isotopically least pure product of any olefin which we examined, and it is the only olefin in which the yield of alkane- d_2 was less than 90% at up to 40°.

The effect of temperature of reaction was investigated over the range of about 40–170° for 2-pentene, cyclopentene and 1-hexene (paper IV,

Table I). The spread in isotopic distributions increases slowly up to 80–90°. At higher temperatures, the isotopic distribution patterns become much broader and highly deuterated species become detectable. Traces of perdeuteriocyclopentane could be detected in the reaction product at 130°. Isotopic exchange of alkane after formation would have occurred in none of our olefin deuteration experiments. The isotopic distribution patterns for deuteration at the higher temperatures resemble those resulting from metallic catalysts. For example, the pattern of run S at 175° with 1-hexene (paper IV, Table I) is rather similar to that with 1-hexene on a nickel-silica catalyst at 105°.²⁰ Reactions at temperatures above 100° were run in an air bath. The heats of hydrogenation may have raised the actual catalyst temperatures substantially above those listed.

The high yield of the product of simple addition of two deuterium atoms to the double bond permits us to test the stereochemistry of hydrogenation on chromium oxide gel in a way which would be impossible on a metallic catalyst.²¹ If two deuterium atoms add *cis* to the double bond, *cis*- and *trans*-2-butene should give the following results:



Deuterogenations of *cis*- and *trans*-2-butene were run at about 0° and the products were analyzed for *meso*- and *dl*-butane-2,3-*d*₂ by infrared absorption spectroscopy. Only the products of pure *cis*- addition could be detected (paper V, section A). It appears that deuteration of 2-butene at about 0° gives at least a 90% yield of the product of simple *cis*-addition to the double bond.

Although one cannot assess the stereochemistry of hydrogenation on metallic catalysts by the addition of deuterium to a secondary olefin, the stereochemistry may be tested by the addition of hydrogen to a tetrasubstituted olefin.²² Previous work has shown that *cis*-addition predominates but that products of net *trans*-addition are often observed. In the attempt to provide some inter-comparison between metallic and chromium oxide gel catalysts, we studied the *hydrogenation* of 1,2-dimethylcyclohexene (paper V, section B). *cis*-Addition would form *cis*-1,2-dimethylcyclohexane, *trans*-addition, *trans*-1,2-dimethylcyclohexane. On chromia, hydrogenation at 100° gives 52% *cis*. Although this product contains much more *cis*-dimethylcyclohexane than corresponds to equilibrium, the stereospecificity is

(20) R. L. Burwell, Jr., and R. H. Tuxworth, *J. Phys. Chem.*, **60**, 1046 (1956), run T, Table II.

(21) J. N. Wilson, J. W. Otvos, D. P. Stevenson and C. D. Wagner, *Ind. Eng. Chem.*, **45**, 1480 (1953). In the deuteration of *cis*-2-butene on a nickel catalyst, C₄H₈D₂ represents but 1/3 of the alkane product even at -78°.

(22) R. L. Burwell, Jr., *Chem. Rev.*, **57**, 895 (1957).

much less than in the addition of deuterium to 2-butene and, we believe, for two reasons. First, in hydrogenating dimethylcyclohexene, dew point considerations required us to work in a temperature range in which addition of deuterium to olefins becomes less specific with respect to alkane-*d*₂ (paper IV, Table I). Secondly, tetrasubstituted olefins hydrogenate more slowly than disubstituted olefins. Accordingly double bond migration is more apt to intrude before hydrogenation.

Isomerization of 1,2-dimethylcyclohexene to 2,3-dimethylcyclohexene gives a product *cis*-addition to which may give either *cis*- or *trans*-dimethylcyclohexane. Hydrogenation of a fraction of dimethylcyclohexene rich in the 2,3-isomer gave the same ratio of *cis*- to *trans*-dimethylcyclohexane as did 1,2-dimethylcyclohexene. It appears probable that the lowered stereospecificity of hydrogenation of 1,2-dimethylcyclohexene results from isomerization to 2,3-dimethylcyclohexene followed by hydrogenation of the latter compound. The intermediates involved in mechanism 4 (section H) may also contribute to this.

E. Double Bond Migration.—Certain details of olefin isomerization were determined to assess any contribution which double bond migration before deuteration might make to the spreading of the isotopic distribution patterns at higher temperatures.

Below 70°, neither isomerization nor exchange of 1-hexene precedes deuteration to any important degree as tested by the examination of unreacted hexene (paper IV, Table II, runs X and Y).²³

At 125°, at half-hydrogenation, the unreacted 1-hexene was slightly more than half-isomerized (run W). At 200°, save for the least active catalyst, unreacted hexene was essentially an equilibrium mixture of 1-hexene and *cis*- and *trans*-2-hexene (runs T, U and V). Perhaps surprisingly, the isomerized olefin averaged less than one deuterium atom per molecule. At 125° (run W), there was but about 1/4 of a deuterium atom per molecule of isomerized hexene assuming that all hexene-*d* was 2-hexene. At 200° (run U), the isomerized hexene averaged about 1/2 of a deuterium atom per molecule. Thus, at temperatures of 125° and above, preliminary olefin isomerization and exchange contributes to the increase in the average deuterium content of the product of deuteration of alkanes; below 70° it contributes negligibly.

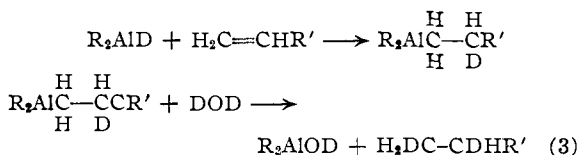
F. Mechanism.—At lower temperatures, the major catalytic processes on chromium oxide gel are those which one might expect on the basis of the most naive view of catalytic activity: isotopic exchange between alkanes and deuterium involves exchange of but one hydrogen atom for each period of adsorption and the addition of deuterium to olefin involves simple *cis*-addition of two deuterium atoms to the double bond. We shall postpone consideration of those minor processes which lead to greater degrees of deuterium introduction until the last section.

Section A presents rather strong evidence against interaction among catalytic sites which must apply

(23) Isomerized or exchanged olefin in the vapor phase is thereby excluded, but not, of course, adsorbed species which never desorb.

eliminating the reverse of reaction 2 in mechanism (2) rather than the diadsorbed alkane itself. Energetics resembling those of the dashed line in Fig. 2 might give such a result. Although it is difficult to decide for or against the presence of such irreversible intermediates, we are inclined to reject the diadsorbed state for two reasons.

First, if a diadsorbed state were possible, it is a little hard to believe that broadening of the simple isotopic exchange pattern would occur nowhere in the rather wide temperature range investigated (200–350°). Yet no deviation from the random distribution is observed in the mono-, di- and tri-deuterohexane. Second, there is a close homogeneous analogy to the olefin deuteration on chromia which, incidentally, dictates the form of mechanism 1 as we present it as against the second and third minor modifications. The addition of diethylaluminum deuteride to 1-alkenes is almost surely a four-center reaction.³² If the diethylaluminum hydroxide could be reduced with deu-



terium to diethylaluminum deuteride, one would have a catalytic deuteration exactly equivalent to that found with chromium oxide. In fact, of course, the diethylaluminum hydroxide undergoes further hydrolysis. Also, a similar mechanism obtains in the addition of diborane to olefins and acetylenes.³³

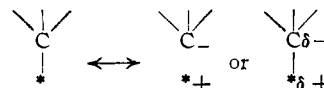
G. Charge Distribution in Carbon-surface Bonds.—Some of our exchange data were acquired to provide information about charge distribution in monoadsorbed alkane, or, more precisely, in the transition state separating alkane and monoadsorbed alkane.

The relative energies of such transition states for a series of alkanes would involve the carbon-hydrogen bond dissociation energies and the charge distribution in the carbon-surface bonds. The first effect gives the sequence for cleavage of R—H bonds, methyl < ethyl < isopropyl < *t*-butyl. Carbonium ion character in the monoadsorbed alkane would lead to the same sequence but in augmented degree. Sufficiently extreme carbanion character would invert the sequence.³⁴

Isotopic exchange between alkanes and deuterium on metallic catalysts follows the bond dissociation energy sequence,³⁵ but there is some evidence that a small carbonium ion contribution may be involved.³⁶ With barium deuteride,³⁷ the carbanion sequence probably obtains.

The exchange of primary hydrogen atoms is preferred on chromia (section B) as on barium

deuteride, whereas, primary hydrogen atoms exchange the least rapidly on metallic catalysts.³⁸ Related to this is the contrast between the relatively rapid exchange of *neopentane* on chromia (paper II, section B) and its slow exchange on metallic catalysts.^{39,40} Also diagnostic is the greater rate of exchange of methane than ethane on chromia (Table I). Some factor must overcome the 5 kcal. greater bond dissociation energy of methane⁴¹ and lead to a general favoring of cleavage of primary carbon-hydrogen bonds. We suggest that monoadsorbed alkane on chromia, although primarily covalent, contains a contribution from the carbanion form



Steric effects may also contribute to this sequence.³⁷

However, the more rapid exchange (Table I) and smaller activation energy for the exchange of hexane as compared with ethane suggests that the degree of carbanion character is not large and that the effect of bond dissociation energy is still quite substantial.

Cyclopropane exchanges much more rapidly than any other hydrocarbon studied (Table I and paper III, section A). Its exchange at 25° is as fast as that at 175° of most other hydrocarbons. The activation energy of exchange 7 kcal. is much lower than with other hydrocarbons.

The bent bond representation of cyclopropane⁴² indicates that the carbon orbitals employed in the carbon-hydrogen bonds are closer to *sp*² than *sp*³. In consequence, the carbon-hydrogen bonds should have a larger bond dissociation energy and the hydrogen atom should be much more acidic than in, for example, cyclopentane. The bond dissociation energy has not been measured but augmented acidity of the hydrogen atoms is in accord with the report that cyclopropane is the only saturated hydrocarbon which has been found to undergo direct transmetalation with amyl sodium.⁴³

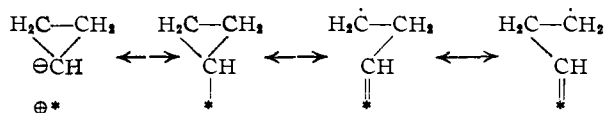
The augmented acidity of cyclopropane and its augmented rate of exchange on chromia are consistent with the assumption of some carbanion character in the transition state and presumably, then, in monoadsorbed cyclopropane. However, the results of exchange of cyclopropane on metals suggest that another effect also enters. Although Addy and Bond⁴⁴ report that hydrogenolysis is much faster than any isotopic exchange on supported catalysts of group VIII, Anderson and Kenball⁴⁵ report that both reactions occur simultaneously on an evaporated rhodium film at -100°. They concluded that cyclopropane undergoes isotopic exchange more rapidly than other satu-

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 (33) H. C. Brown and G. Zweifel, *THIS JOURNAL*, **81**, 247, 1512 (1959).
 (34) H. Pines and V. Mark, *ibid.*, **78**, 4316 (1956); H. Pines and L. Schaap, *Advances in Catalysis*, **12**, (1960).
 (35) R. L. Burwell, Jr., B. K. C. Shim and H. C. Rowlinson, *THIS JOURNAL*, **79**, 5142 (1957).
 (36) J. M. Forrest, R. L. Burwell, Jr., and B. K. C. Shim, *J. Phys. Chem.*, **63**, 1017 (1959).
 (37) L. Wright and S. Weller, *THIS JOURNAL*, **76**, 5048 (1954).

(38) Ref. 26, pp. 323 and 334.
 (39) C. Kembal, *Trans. Faraday Soc.*, **50**, 1344 (1954).
 (40) H. C. Rowlinson, R. L. Burwell, Jr., and R. H. Tuxworth, *J. Phys. Chem.*, **59**, 225 (1955).
 (41) D. P. Stevenson, *Discussions Faraday Soc.*, **10**, 113 (1951).
 (42) C. A. Coulson and W. E. Moffit, *Phil. Mag.*, **40**, 1 (1949).
 (43) L. J. Lampher, L. M. Redman and A. A. Morton, *J. Org. Chem.*, **23**, 1370 (1958).
 (44) J. Addy and G. C. Bond, *Trans. Faraday Soc.*, **53**, 388 (1957).
 (45) J. R. Anderson and C. Kembal, *Proc. Roy. Soc. (London)*, **226A**, 472 (1954).

rated hydrocarbons. This suggests that the conjugative ability of cyclopropane^{42,46} is involved on both types of catalysts.

One may employ isovalent hyperconjugation⁴⁷ with both types of catalysts although the situation is unusual in that the double bond between carbon and surface site would probably be a *d-p* π -bond.



Similar conjugative stabilization of reacting cyclopropane cannot occur during addition to cyclopropane rings. Very probably for this reason, isotopic exchange occurs with a lower activation energy than hydrogenolysis (section C), although the exchange reaction is thermally neutral while the hydrogenolysis reaction is exothermic by nearly 40 kcal. The hydrogenolysis reaction on chromia may well proceed as a four-center reaction between cyclopropane and Cr-H to form monoadsorbed propane. In this, a σ -bond in cyclopropane is opened in much the same way as a π -bond in our mechanism (1).

H. Multiple Exchange Processes.—The salient features of those processes which lead to the formation of more highly deuterated species in alkane exchange and olefin deuteration are.

(a) The relative rates of simple exchange, of extensive multiple exchange and of excess D_2 and D_3 vary from reactivation to reactivation (section B).

(b) The ratio of extensive multiple to simple exchange increases in the sequence cyclohexane, cyclopentane, cycloheptane, cyclooctane (paper III, Table III) as does the preponderance of perdeuteriocycloalkane.

(c) As with metallic catalysts,⁴⁸ extensive multiple exchange exhibits a large maximum at the perdeuteriocycloalkane (paper III, Table III) but hexane maximizes at D_{12} (paper III, Table V).

(d) The fraction of (+)3-methylhexane molecules which racemizes during isotopic exchange with deuterium is about equal to that which undergoes extensive multiple exchange (paper V, section C).

(e) Only the cycloalkanes exhibit excess D_2 and D_3 (section B).

(f) With cyclohexane, the activation energy is about 16 kcal. for the three processes: simple exchange, extensive multiple exchange and excess D_2 and D_3 (paper III, section C).

(g) 2,3-Dimethylbutane gives an exchange pattern characterized by a small value for D_4 , large values for D_5 to D_8 , small values for D_9 to D_{11} and large values for D_{12} to D_{14} (paper III, Table IV).

(h) The isotopic distribution patterns of the products of olefin deuteration are the same on slightly and on fully activated catalysts.⁴⁸

(i) Despite the spread in the isotopic distribution pattern, the average deuterium content of the prod-

uct of addition of deuterium to the olefin at 40° is very close to 2.00. The average content rises rapidly above 100° (paper IV, Table I).

(j) In the temperature range, 125 to 200°, deuterium introduction accompanies double-bond migration (a side reaction to olefin deuteration) only one-quarter to one-half of the time (section E).

(k) Activity for olefin isomerization increases much more slowly with activation of a catalyst than does that for olefin hydrogenation (section A).

(l) One of our most used catalysts contained 40 parts per million of iron, 5 of nickel and less than 5 of cobalt (paper III, Techniques).

Several of these items are suggestive of a catalyst with at least two types of sites. Some, items (c) and (d) particularly, might result from contamination by metals formed by reduction of impurities. However, metallic catalysts should lead to extensive multiple exchange with ethane²⁸ and to smeared isotopic distribution patterns in deuterated ethylene.²⁹ Since neither is observed (sections B and D, respectively) and since metal contamination is very small (l), we feel that most or all of the listed items are probably inherent in chromium oxide itself.

The occurrence of reaction on two types of sites is established for double bond migration (k) and suggested for extensive multiple exchange (a). However, whatever process leads to the smearing of the isotopic distribution patterns during olefin deuteration, probably occurs on the same sites as olefin deuteration itself (h) since equal rates of formation of two different types of sites during activation is somewhat unlikely.

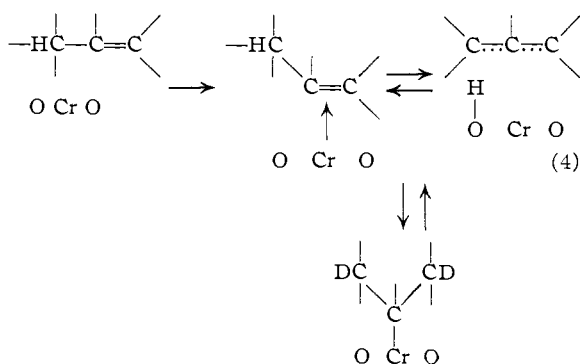
As reported in Section A, there is rather strong evidence against interaction between adsorbed alkyl groups. If one accepts this, reaction at any one pair site should be independent of the degree of coverage of the other sites. As the isotopic exchange experiments show, a monoadsorbed alkane is unlikely to engage in any reaction other than mere desorption. This should apply to any α -monoadsorbed β -deuterioalkane formed during olefin deuteration. Yet, at 170°, the deuteration of olefins leads to a very wide isotopic distribution pattern, whereas alkanes indulge in simple exchange almost exclusively. Therefore, whatever process leads to wide distribution patterns in olefin deuteration precedes the formation of monoadsorbed alkane yet does not involve vapor phase olefin (since unreacted olefin is neither isomerized nor exchanged below 70°). The exclusive formation of ethane- d_2 in the deuteration of ethylene implicates an allylic hydrogen atom as involved in forming the wide distribution pattern.

Any mechanistic proposals which we can offer for most of the listed items are both incomplete and speculative. The following mechanism is, however, a possibility and we leave it in as general a form as possible. The initial form of adsorption of olefin might be considered a π -complex. The other form is an adsorbed allyl radical or ion. It might be adsorbed either as written by involvement of the three *p*-orbitals or it might be of the

(46) J. P. Friend and B. P. Dailey, *J. Chem. Phys.*, **29**, 577 (1958).

(47) N. Muller and R. S. Mulliken, *THIS JOURNAL*, **80**, 3489 (1958).

(48) The isotopic distribution patterns of hexanes in runs W (125°), X (72°) and Y (55°) in which the degrees of hydrogenation were about one-half (paper IV, Table II) differ negligibly from runs on completely activated catalysts at corresponding temperatures.



form, $\text{Cr}-\text{C}-\text{C}=\text{C}$. In either case, alternation between adsorbed olefin and adsorbed allyl permits multiple exchange *via* migration of the position of adsorption. One must assume that the rates are such that there is negligible return of olefin to the vapor phase. Mechanism 4 modifies mechanism 1 by adding intermediates which intervene between gas phase olefin and mono-adsorbed alkane. These intermediates substitute for the diadsorbed alkane in mechanism 2.

At lower temperatures, the spread in the isotopic distribution patterns is unaccompanied by increase in average deuterium content (i). If one rejects direct interaction among adsorbed hydrocarbon fragments, one must conclude that *exchange* between adsorbed hydrogen atoms and gas phase deuterium is slow relative to deuterogenation of olefin. However, although the rate of desorption of hydrogen(deuterium) is slow, the rate of surface migration of hydrogen or deuterium atoms could be relatively fast. Thus, with an appropriate relationship of rate constants, mechanism 4 can widen the isotopic distribution pattern without altering the average deuterium content.

This relationship in rates would not be expected in alkane exchange: the exchange reaction is much slower than hydrogenation and operating temperatures are higher. Further, at least on whatever sites lead to multiple exchange, exchange between hydrogen atoms on the surface and deuterium molecules in the gas must be relatively fast or one could not obtain perdeuterocycloalkanes as major products (c).

The absence of multiple isotopic exchange in ethane suggests that multiple exchange, in general, proceeds by a mechanism similar to that just described. Here, however, adsorbed olefin is not in the direct line of reaction but, rather, in a side reaction which is probably endothermic and which occurs with low probability on most sites. Thus, little mono-adsorbed alkane reacts to form adsorbed olefin but, if that little rapidly alternates with adsorbed allyl and if rapid exchange occurs between adsorbed hydrogen atoms and gas phase deuterium, one obtains the observed results, simple exchange plus a small amount of extensive multiple exchange.

The sequence of the degrees of extensive multiple exchange in cycloalkanes (b) and of the relative concentration of perdeuterioalkane in the multiply exchanged product (b) is the same as the sequence of decreasing heats of hydrogenation of cycloalkenes.⁴⁹ This accords with the mechanism.

Although equilibrium with desorbed olefin could lead to extensive multiple exchange and satisfy item d, energetic considerations render this improbable. The activation energy of extensive multiple exchange cannot exceed 16 kcal. by very much (f), yet the endothermic heat of reaction to cyclohexene, for example, is 28 kcal. Further, the absence of extensive multiple exchange in ethane is incompatible with olefin.

Racemization of (+)3-methylhexane (d) and the predominance of perdeuteriocyclopentane in the multiply exchanged portion of exchanged cyclopentane (c) requires some kind of symmetric intermediate or transition state.³⁵ In the proposed mechanism, adsorbed olefin or adsorbed allyl might be adsorbed in some symmetric fashion or the adsorbed species might be able to turn over.

The apparent inconsistency in our proposals introduced by items (a) and (h) may be resolved as follows: Any process of site generation may very well lead to sites of slightly different geometry on which the relative rates involved in the proposed mechanism would be somewhat different. The results of such differences would be much more noticeable in alkane exchange where the important variable is the probability of forming adsorbed olefin from mono-adsorbed alkane than in the deuterogenation of olefin in which case adsorbed olefin is in the direct line of reaction.

Diffusion limitation cannot cause the extensive multiple exchange in alkanes. The rate of diffusion of deuterium is but five times that of cycloheptane. This would not permit formation of such an overwhelmingly predominant amount of perdeuteriocycloheptane (paper III, Table III). We cannot eliminate the possibility of a process limited by diffusion in the case of the much more rapid deuterogenation of olefin although item (h) constitutes an argument against this.

Olefin isomerization must occur, at least in part, upon sites different from those involved in deuterogenation (k). The presence on the surface of considerable amounts of hydrogen atoms produced by exchange accompanying deuterogenation can account for isomerized but unexchanged olefin (j). Our data upon olefin isomerization are too meager to warrant further discussion.

Acknowledgment.—Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for the support of the research reported in this series of papers.

(49) The heats of hydrogenation of cyclohexene, cyclopentene, cycloheptene and cyclooctene are 28.6, 26.9, 26.5 and 23.5 kcal. per mole, J. B. Conn, G. B. Kistiakowsky and E. A. Smith, *THIS JOURNAL*, **61**, 1868 (1939).