

be 44 ± 3 kcal.²¹ We are now in a position to make an estimate of the resonance energy in diborane. Let us first consider the reaction $B(s) + 1\frac{1}{2}H_2 = BH_3(g)$. Since the electronegativities of boron and hydrogen are identical for purposes of calculation there are no heat effects due to the ionic contributions of the bonds. Hence if the solid consists of boron atoms which are bonded to three others by single bonds it is clear from Pauling's additivity rule that the above reaction will be accompanied by a zero heat effect since for every B-H bond which is formed one-half an H-H and one-half a B-B bond will be broken. On the other hand, it appears quite likely that in the solid the boron atoms are tetrahedrally bonded, thus making use of all the orbitals available to them by means of some resonance scheme; then more bonds will be broken in the vaporization process than will be formed in the hydrogenation. Consequently the reaction giving rise to BH_3 radicals will be endothermic by an amount equivalent to the resonance energy present in solid boron. But the heat of formation of diborane from the elements was found to be exothermic. Hence we must conclude that the reaction $2BH_3 = B_2H_6$ is exothermic to the extent of 44 kcal. if the first alternative is assumed or to the extent of 44 kcal. plus the resonance energy available for each pair of atoms in solid boron if the second is preferred.

The stability of B_2H_6 relative to BH_3 or B_2H_4

(21) W. A. Roth and E. Börger, *Ber.*, **70**, 48 (1937).

is due to the resonance energy made possible in the former compound by the complete use of all the four orbitals permitted to boron atoms. From the arguments presented in the preceding paragraph we may estimate that a minimal value for this energy is 44 kcal. and may be set equal to the latter figure plus the resonance energy for a pair of boron atoms in the solid element.

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Summary

Electron diffraction photographs of diborane indicate that this compound has an ethane-like structure with the B-B distance equal to 1.86 ± 0.04 Å. and the B-H distance 1.27 ± 0.03 Å.; the valence angles of the boron atoms are found to be tetrahedral within three degrees. An electron configuration compatible with the large interatomic distances is presented both in terms of the atomic and molecular orbital modes of description and the conclusion is reached that the stability of B_2H_6 relative to BH_3 is due to the resonance energy made available through the full use of the four orbitals of boron.

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The Activation of Specific Bonds in Complex Molecules at Catalytic Surfaces. III. The Carbon-Hydrogen and Carbon-Carbon Bonds in Propane and Ethylene

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The present research represents an extension to propane and ethylene of investigations previously reported by Morikawa, Benedict and Taylor dealing with methane³ and ethane.⁴ In the latter communication attention was directed to an abnormally high inhibitory action of hydrogen on the surface hydrogenation decomposition of ethane to yield methane. We have examined

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(3) Morikawa, Benedict and Taylor, *THIS JOURNAL*, **58**, 1445 (1936).

(4) Morikawa, Benedict and Taylor, *ibid.*, **58**, 1795 (1936).

in the present work, in a more detailed manner, the kinetic relations of the decomposition and exchange reactions between propane and deuterium with results which confirm and extend our observations with ethane. Isotope exchange reactions with ethylene are also included as well as other supporting studies leading to a general discussion of the whole problem of activation in such hydrocarbon systems.

Experimental Details

Materials.—In addition to those gases described in the previous papers,^{3,4} we have employed propane, ethylene

and propylene. In each case the gases were obtained from cylinder supplies and purified by repeated fractionation. With propane the only likely impurity in the purified sample would be a trace of butane. The ethylene was 100% C₂H₄, within the analytical error. The propylene analyzed 98% C₃H₆, 2% C₃H₄.

Experimental Method.—A static method was employed, essentially the same as that described in Part II but of ~135 cc. reaction volume. After definite reaction times the products were removed by a Töpler pump. About 95% of the gas could thus be removed within five minutes, but fifteen minutes were required to remove all the gas. Temperature control of the reaction was by means of vapor baths.

Analytical Procedure.—Hydrogenation decomposition was followed by the increase in saturated hydrocarbon, +ΔH.C. after removal of hydrogen by combustion over copper oxide at 230°. In some cases, a fractionation method was employed to define the composition of the hydrocarbon products.

The isotope exchange reaction was followed by a determination of the C-D content of the hydrocarbons. This was checked occasionally by the D content of the hydrogen. Both analyses were made with a thermal conductivity gage to be described elsewhere.⁵ An accuracy of 0.5% in the analyses of the ethanes and propanes and 0.1% for the hydrogens was possible.

Propane and ethane were separated from hydrogen by passage through a liquid-air trap. Traces of hydrogen were removed from the condensate by repeated vaporizations, freezings and evacuations at liquid-air temperature. The final purification of the gases for analysis was by fractional distillation under reduced pressure (~2 mm.). Details of this fractionation technique will be described in a separate communication⁶ since it has general applicability and is essential to our method of analysis by thermal conductivity.

Experimental Results

Exchangeable Hydrogen in a Nickel-Kieselguhr Catalyst.—It was necessary to determine the extent to which deuterium would exchange with hydrogen sources in a nickel-kieselguhr catalyst in the ranges of temperature in which exchanges with hydrocarbons occur. Two series of experiments detailed in Table I were performed. The same catalyst, 2 g. in weight, ~15% Ni, was used in both series. The catalyst was prepared from nickel carbonate precipitated on kieselguhr, by reduction for four hours at 425° followed by evacuation with a mercury diffusion pump system for two hours at the same temperature. Between each experiment the catalyst was washed thoroughly with hydrogen at the reaction temperature and then evacuation, for intervals of time noted in the table, followed. Then ~23 cc. of deuterium was introduced.

(5) N. R. Trenner, *J. Chem. Phys.*, forthcoming paper.

(6) Morikawa and Trenner, *THIS JOURNAL*, forthcoming paper.

After definite time intervals the gas was recovered by a Töpler pump and analyzed on the thermal conductivity gage. The experiments in Series II were made after the catalyst had been changed in activity by heating to 500° with evacuation.

These experiments lead to the following conclusions. From Expts. 51 and 52 it is evident that one hour of evacuation is adequate and that equilibrium is also established in one hour. From Expts. 58 and 59 we conclude that thirty-six minutes is not sufficient for equilibrium at 302°. Experiments 53 and 60 show that evacuation at 302° decreases the hydrogen content by 5.5%, but this is still only a fraction of the hydrogen available at 98°. On the other hand, it removes all of the hydrogen available at 55° (see Expts. 104 and 111).

TABLE I
HYDROGEN SOURCES OF NICKEL-KIESELGUHR CATALYST

Order of expt. no.	Temp. of wash- ing and evacu- ation, °C.	Time of last evacu- ation, hrs.	Reaction Temp., °C.	Time, hrs.	D ₂ introduced, cc.	Gas recov- ered, cc.	D con- tent of re- covered gas, %	Amt. of H ₂ source (K = 1), cc.
Series I								
51a	55	7.5	55	8.3	22.9	21.3	83.4	4.3
b	55	..	55	1.0	22.9	23.1	96.0	..
52a	55	1.0	55	1.0	23.3	22.6	83.0	4.5
b	55	..	55	2.0	23.0	22.9	95.0	..
53	98	3.1	98	1.0	22.9	21.7	82.0	4.8
54	138	2.0	138	1.0	23.2	22.3	76.9	6.7
55	172	2.8	172	1.0	23.4	21.8	71.7	8.9
56a	218	2.0	218	1.0	23.1	21.9	58.8	15.8
b	218	..	218	1.5	23.2	23.2	82.4	..
c	218	..	218	1.0	22.8	22.8	90.7	..
57	255	2.0	255	0.6	23.3	22.4	53.8	19.7
58	302	2.0	302	.6	23.7	22.9	44.3	30.1
59	302	2.1	302	5.2	23.5	22.5	38.9	36.4
60	302	2.0	98	4.0	22.9	19.6	87.5	3.0
Series II								
102	450	4.0						
	500	4.0	218	3.5	23.2	19.1	69.8	9.7
103	218	2.0	218	2.0	23.6	22.5	69.7	9.8
104	55	2.0	55	2.0	23.1	22.0	86.2	3.3
110	0	2.0	0	2.0	23.6	22.8	86.2	3.4
111	302	2.0	55	2.0	23.6	20.3	96.2	0.6

Experiments labelled a, b, c referred to successive experiments without intermediate washing and evacuation.

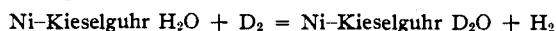
From the whole series (51-60) we conclude that the amount of hydrogen available increases as the temperature rises, but that the data detailed above indicate two types of available hydrogen, one readily removed by evacuation at high temperature, the other not so removable.

Prior to Expt. 102 four hours of evacuation at 450° yielded 8.4 cc. of water vapor and a further four hours at 500° gave an additional 8.5 cc. After this removal the hydrogen content of the wash gas decreased by 11% at 218° but only by 3% at 55° (*cf.* Expts. 51, 52, 104). From the data of Expts. 102, 103 it is obvious that evacuation at 218° removes all of the more readily available hydrogen.

Assuming an equilibrium constant of 1 between deuterium and the hydrogen source on the catalyst the values for this source are given in the final column of Table I, and represented in curve A, Fig. 1. The calculations are made with the aid of the equation

$$\text{Cc. of available H}_2 = \frac{\text{cc. of D}_2 \text{ introduced (99\% D found)}}{\% \text{ D found}}$$

The same volume of hydrogen is recoverable at 218° as at 55°. Experiments detailed in Table II indicate that, in this range of temperature, the activated adsorption of hydrogen decreases as the temperature rises. The amount adsorbed at 0.15 mm. pressure was found to be ~5.5 cc., a value to be compared with 4.5 cc. available at 55° with an evacuation pressure of 10⁻³ mm. as revealed by the exchange reaction. We therefore conclude that the available hydrogen which can be evacuated at 55° is hydrogen gas and that the other available hydrogen which is difficultly removable at higher temperatures results from water. We further conclude that this water does not exist on the nickel surface but is present in the kieselguhr support, the silicates of which hold water with varying degrees of tenacity. These hydrogen sources are quite reproducible and so point to the establishment of equilibria of the type



The experimental value of the total available hydrogen at 218° is ~16 cc., which is in agreement with the calculated value of 16 cc. assuming an equilibrium constant $K = 1$. If we use the constant $K = 1.46$ obtained from Farkas' data⁷ for the equilibrium between free water and deuterium, a calculated value of 13.6 cc. of available hydrogen would be obtained. We may ascribe the difference in equilibrium constants to the existence of hydrated kieselguhr as the water source.

These conclusions are substantiated by the following two series of experiments. A 2-g.

(7) Farkas, "Light and Heavy Hydrogen," p. 180, *et seq.*

sample of fresh unreduced catalyst was heated to 425° with evacuation and held at that temperature for two hours. It was then cooled and washed with deuterium at room temperature. The catalyst was then gradually raised in temperature in a stream of deuterium to 400°, samples of gas being withdrawn at intervals and analyzed. The deuterium consumed in the reduction was 66.3 cc. and the water frozen out in a carbon dioxide trap corresponded to 60.2 cc.

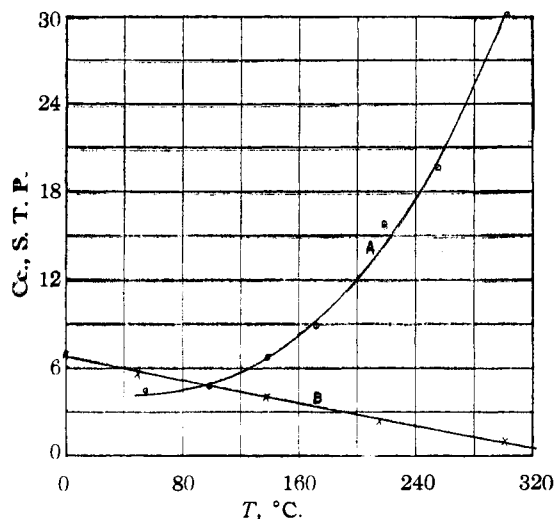


Fig. 1.

The hydrogen received in the deuterium gas amounted to 16.8 cc. The hydrogen content of the water condensed out was determined by equilibrating the water vapor with deuterium on the catalyst at 138°. In this manner, using $K = 1.46$, we determined in all 22.4 cc. of hydrogen in the water and a total hydrogen in both gas and water of 16.8 + 22.4 = 39.2 cc. If we use $K = 1$ the corresponding amounts are 16.8 + 31 = 47.8 cc., which values determine the upper and lower limits for the total hydrogen.

The catalyst was then evacuated for two hours at 138° and 56.8 cc. of water vapor was frozen out in the carbon dioxide trap. The catalyst was then well washed with hydrogen at 218° and evacuated for ten hours at the same temperature. The water removed was 7.7 cc., making a total recovered water of 64.5 cc. The close correspondence of this with the deuterium consumption, 66.3 cc., indicates that almost all the water produced in the reduction process could be desorbed at 218°. This implies that the water available in the experiments of the first two series is not water on the nickel surface but in the kiesel-

guhr. This was confirmed by introducing 22 cc. of deuterium gas, equilibrating for three and a half hours at 218° when, after evacuation, the desorbed gas contained only 37% deuterium corresponding to a source of 34 cc. of available hydrogen.

Adsorption Isobars ($p \sim 0.15$ mm.) of Deuterium on Nickel.—The nickel catalyst was evacuated at a temperature T_1 for about twenty minutes by the Töpler pump and the pressure (P_1) built up in the next thirty minutes was measured. The temperature was then raised to T_2 and the pressure (P_2) was read. The desorbed deuterium (ΔD_2) was measured and the pressure (P_3) built up on standing for one-half hour was noted. These operations were repeated from -83 to 302° . The data obtained are shown in Table II.

TABLE II

ISOBAR OF D_2 ON Ni CATALYST AT ~ 0.15 MM. PRESSURE

T_1 , °C.	P_1 at T_1 , mm.	T_2 , °C.	P_2 at T_2 , mm.	ΔD_2 , cc.	P_3 at T_2 , mm.
0	0.18	55	2.1	1.39	0.14
55	.14	138	4.0	1.65	.16
138	.16	218	3.2	1.56	.18
218	.18	302	3.8	1.30	.10
-83	.58	23	18.7	5.03	.42
-24	..	22.4	3.9	1.29	.25
-83	.16	21.3	9.1	2.88	.25

Evacuation for twenty minutes with the Töpler pump corresponds approximately to evacuation for five minutes with our mercury diffusion pump train. A plot of deuterium adsorbed against temperature shown in Fig. 1 shows a decreasing hydrogen adsorption with increasing temperature, curve B, Fig. 1.

The Hydrogenation Decomposition of Propane.—The experimental data on the conversion of propane and hydrogen to ethane and methane are collected in Table III.

The original catalyst, as for the experiments in Table I, was used. It will be seen that the reaction acquires an appreciable velocity at 138° , which is about 10° lower than in the case of ethane. The decomposition with deuterium was again slower than that with hydrogen, as with ethane. The fractional analyses of the hydrocarbon products, given in Table IV, shows that the initial reaction yields ethane and methane and that the ethane thus formed decomposes further to methane, but not to an appreciable extent under the majority of our conditions. We,

therefore, represent the total over-all reactions, thus

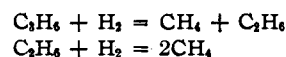


TABLE III

HYDROGENATION DECOMPOSITION OF PROPANE

No.	Propane, cc.	H_2 , cc.	Temp., °C.	Time, hrs.	$+\Delta H.C.$, %	$\% \Delta H.C.$ per hr.
36	11.5	23.3	138	10.3	22.9	2.2
35	11.4	22.9	157	3.0	39.3	13.1
37	11.5	23.3	172	1.1	69	63
38	11.4	23.1	184	1.1	≥ 190	
39	11.4	23.4	157	3.0	34.4	11.5
40	11.5	23.5(D_2)	157	3.0	19.9	6.6
41	11.4	23.7	157	3.0	32.3	10.8
42	11.5	46.2	157	8.0	17.5	2.2

TABLE IV

FRACTIONATION OF HYDROCARBON PRODUCTS

No.	$+\Delta H.C.$, cc.	CH_4 , cc.	C_2H_6 , cc.	C_3H_8 , cc.
41	3.7	4.2		
42	2.0	2.2		
100	5.3	6.2	4.2	8.7

Kinetics.—The kinetic studies were made at three temperatures and are summarized in Table V. Figure 2 shows the comparative rates of the

TABLE V

KINETICS OF HYDROGENATION DECOMPOSITION OF PROPANE

No.	C_3H_8 , cc.	H_2 , cc.	Temp., °C.	Time, hrs.	$+\Delta H.C.$, %	Con- version % per hr.
87	23.2	47.0	138	23.0	6.8	0.30
88	11.5	35.4	138	13.2	8.8	.67
89	11.5	23.2	138	5.0	10.2	2.04
90	17.4	35.3	138	14.0	8.9	0.63
83	23.0	46.8	157	5.0	12.1	2.4
84	23.3	71.7	157	13.0	9.5	0.73
85	11.4	23.3	157	1.1	13.1	11.9
86	11.3	53.2	157	5.0	9.2	1.8
91	22.9 + 25.0 (CH_4)	46.4	157	7.0	13.6	1.9
93	22.8 + 23.0 (C_2H_6)	46.0	157	7.4	8.5	1.2
92a	23.1	46.3	172	0-1.1	14.5	13.2
b				-3.8	43.1	11.3
c				-6.8	87.8	12.9
94	23.0	69.6	172	3	13.5	4.5
95	22.9	46.4	172	1	13.6	13.6
96	11.5	46.3	172	1	14.3	14.3
100	13.8	28.0	172	1	38.5	38.5

ethane and propane reactions. With propane as with ethane the rate of decomposition increases slightly with time. Analysis of the rate measurements indicates a reaction strongly inhibited by hydrogen and weakly by hydrocarbon products, the numerical data yielding the values presented in

Table VI. From the temperature coefficient of the process we deduce an activation energy of ~ 34 kcal.

TABLE VI
KINETICS OF HYDROGENATION DECOMPOSITION

$$k \propto (C_3H_8)^x (H_2)^y (C_2H_6)^z (CH_4)^w$$

Temp., °C	x	y	z	w
138	+0.91	-2.70
157	+ .94	-2.43	-0.24	-0.07
172	+ .90	-2.66

On the average, $k \propto (C_3H_8)^{+0.92} (H_2)^{-2.6}$

The Exchange Reaction of Propane and Deuterium: (a) Equilibrium.—The catalyst was washed first with $2H_2 + 1D_2$ and then experiments were made with $C_3H_8 + 2D_2$ mixtures. Before Expts. 64 and 65 the wash gas was $1H_2 + 1D_2$, and before Expt. 74 the wash gas was pure D_2 . The data are presented in Table VII.

TABLE VII
EQUILIBRIUM OF EXCHANGE REACTION

No.	C_3H_8 , cc.	D_2 , cc.	Temp., °C.	Time, hrs.	% D in H_xD_y	% C-D in $C_3H_xD_y$	$K = \frac{CD}{CH} \times \frac{H}{D}$
68	11.6	23.4	65	10.3		39.8	
69	11.6	23.5	65	3.0		20.9	
48	11.6	24.1	80	6.0		36.8	
49	11.7	24.1	80	13.0		39.3	
73	11.6	23.5	80	11.0	24.7	45.6	2.57
50	11.7	23.7	98	3.8	21.8	39.4	2.33
62	11.6	23.5	98	4.2	23.3	41.2	2.31
63	11.5	22.6	98	5.2	22.5	40.9	2.38
65	11.6	45.6	98	1.1		44.8	
64	11.5	45.6	98	5.1	40.2	61.0	2.32
46	11.6	23.7	110	1.1		40.4	
47	11.6	23.6	110	3.0		38.6	

In addition to the hydrocarbon exchange in this system there is, as pointed out in an earlier section, another source of exchange, namely, the kieselguhr support. Therefore, the hydrocarbon concentrations of equilibrium mixtures depend on the previous history of treatment of the catalyst. Exact equilibrium constants require, therefore, analysis of *both* hydrogen and hydrocarbon contents of the equilibrium mixture. In the experiments for which these analyses are available satisfactory constants are obtained with mean values, $K_{98} = 2.34$ and $K_{90} = 2.57$. From these we deduce a heat of reaction of 1.4 kcal.

(b) Kinetics.—In the kinetic experiments the catalyst was washed with deuterium before each run. The initial condition of the catalyst was therefore identical in all runs. The variation in the C-D percentage is undoubtedly the better way to measure the rate of reaction because, as

the last column in Table VIII shows, lower values of exchange in the hydrogen occur due to the existence of the water-deuterium exchange.

TABLE VIII

No.	C_3H_8 , cc.	D_2 , cc.	Temp., °C.	Time, hrs.	% D in H_2D_2	% CD in $C_3H_xD_y$	% C-D per hr.	H ex-changed, cc.	C-D ex-changed, cc.
79	11.3	22.7	21.5	7.0	78.1	13.4	0.19	9.5	12.1
74	11.5	45.8	65	2.0	85.8	13.0	6.5	12.1	12.0
75	11.4	22.9	65	1.0	81.0	11.1	11.1	8.3	10.1
76	22.8	46.0	65	2.0	80.7	10.0	5.0	16.9	18.2
77	11.4	11.5	65	0.5		9.6	19.2		8.7
78	11.5	23.6	65	1.0	82.4	10.4	10.4	7.8	9.6
69	11.6	23.5	65	3.0		20.9	7.0		19.4
70	11.6	23.6	80	1.0		24.5	24.5		22.7
71	11.6	55.0	80	2.0		27.0	13.5		25.1
80	11.4	22.8	80	0.5	73.6	17.2	34.4	11.6	15.7

The exchange reaction with propane occurs at temperatures $\sim 40^\circ$ lower than that with ethane.

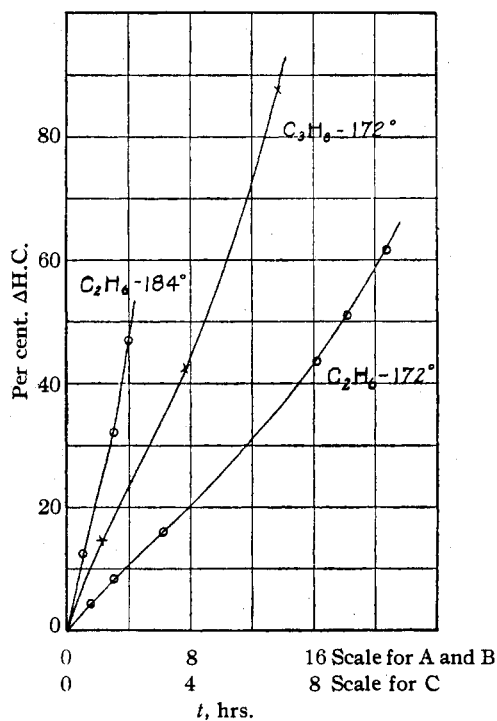


Fig. 2.

The activation energy of the process, ~ 19 kcal., is again much smaller than the value of ~ 34 kcal. found for the hydrogenation decomposition process. The inhibiting effect of hydrogen is also much less marked than in the decomposition process, the kinetics following the equation, $k \propto (C_3H_8)^{0.62} (D_2)^{-0.76}$, in contrast to $(H_2)^{-2.6}$ in the decomposition reaction. We refer to this point later.

Preparation of Propane- d_8 .—The previous data suggested the following method of prepara-

tion of C_3D_6 . A mixture of 22.6 cc. of C_3H_8 and 45 cc. of D_2 was left in contact with the nickel catalyst for three hours at 98° and then the equilibrated propane was separated in a liquid air trap. The propane thus recovered was subjected to six further successive treatments with deuterium under similar conditions. In the sixth conversion the deuterium recovered was 95% D. In the seventh it was 97.5% D. From the equilibrium constant $K_{98^\circ} = 2.34$ this value corresponds to a propane of C-D content 98.9%. The product was fractionated under reduced pressure to remove a trace of ethane- d_6 . The gas was then analyzed in the thermal conductivity gage. The properties of this preparation will be described elsewhere.

Hydrogenation of Ethylene.—The interaction of hydrogen and ethylene on the nickel catalyst under the conditions specified in Table IX showed no breaking of the carbon-carbon bond up to a temperature of 138° and was the straight hydrogenation.

TABLE IX

No.	C_2H_4 , cc.	H_2 , cc.	Temp., $^\circ C.$	Gas recovered, cc.	H.C. (C_2H_4), cc.
24	18.5	37.4	20	38.0	18.4
25	18.9	38.7	80	38.7	18.9
101	19.9	44.2	138	44.2	20.1

Experiments with deuterium are recorded in Table X. The catalyst was again that used in the experiments of Table I. Experiment 82 is not comparable with Experiments 107–112 in which latter group the activity of the catalyst was changed due to a previous heat treatment. The comparison experiments were with a copper catalyst obtained by alternate reduction and oxidation of copper oxide granules (1.5 g.) with a final reduction and evacuation at 270° . The catalysts were in all cases well washed with deuterium.

TABLE X

REACTION OF ETHYLENE AND PROPYLENE WITH D_2 ON Ni AND Cu CATALYST

No.	Catalyst	C_2H_4 , cc.	D_2 , cc.	Temp., $^\circ C.$	% D in H_2D_2	% C-D in H.C.	C-D ex- changed, cc.	% ex- change in C-H of C_2H_4
81	Ni	19.7	47.6	20	91.4	35.7	3.3	4.3
112	Ni	19.8	38.9	-80	97.1	33.4	0.6	0.8
107	Ni	19.5	39.7	-24	89.8	36.7	4.4	5.8
108	Ni	19.5	41.4	65	82.8	39.7	8.0	10.3
113	Cu	19.4	38.5	0	91.8	35.1	2.6	3.4
		C_3H_6						
115	Cu	19.0	40.4	0	83.8	28.5	6.5	5.7

On nickel the rate of hydrogenation was very rapid throughout the whole temperature range studied, -80 to 65° . Reaction at each temperature was complete within fifteen minutes. On the copper catalyst about one hour and a half was required at 0° . On this catalyst the amounts of hydrogen and saturated hydrocarbon adsorbed are very small and the catalytic hydrogenation can be used for analytical determinations of ethylene and propylene in gaseous mixtures.⁶

If no exchange reaction occurred between ethylene and deuterium the C-D concentration in the ethane obtained would be 32.9 and 24.2% if propylene were converted to $C_3H_6D_2$ since the deuterium content of the gas used was 98.7% D. Excess C-D percentages in the product indicate exchange.⁸ The eighth column of Table X shows the results of calculations of exchange on this basis, expressed as cc. of C-D bonds, to be compared with the amount of hydrogenation, expressed also as cc. of C-D bonds, in each experiment approximately 39 cc. It will be observed that the C-D bonds produced by exchange increase with the temperature, that the activation energy of exchange is higher than that of hydrogenation and that the former is slower than the latter throughout our temperature range. These conclusions are different from those reached by Farkas, Farkas and Rideal.⁹

The copper catalyst becomes, consequently, a most convenient contact agent on which to prepare partially exchanged ethanes and propanes of known deuterium content from controlled mixtures of ethylene or propylene and deuterium, since the amounts of residual adsorption of hydrogen and hydrocarbon on copper after evacuation are negligibly small and exercise no measurable effect on the composition of the mixture introduced.

Polymerization of Ethylene.—The nickel catalyst used in the preceding experiments was evacuated for one and a half hours at 340° , 19.9 cc. of ethylene was introduced at 23° and left in contact for thirteen hours. The amount of permanent gas ($H_2 + CH_4$) produced was negligible. The gas recovered by freezing-out in a liquid air trap had a volume of 11.5 cc. This recovered gas was fractionated under a reduced pressure and found to contain 8.8 cc. of a C_2 -fraction, a negli-

(8) Wheeler and Pease [THIS JOURNAL, **58**, 1665 (1936)] found no exchange.

(9) Farkas, Farkas and Rideal, *Proc. Roy. Soc. (London)*, **A146**, 680 (1934).

gible amount of C₃-fraction and 2.7 cc. of a C₄- or higher fraction. By hydrogenation with the copper catalyst the C₂-fraction proved to be 86% ethylene and 14% ethane. The higher fraction was hydrogenated to methane at 300° on nickel and the average number of carbon atoms in the molecule was found to be 4.17.

The gas left on the original catalyst after the liquid-air removal process was converted on the catalyst to methane with hydrogen at 300°. Methane to the extent of 9.6 cc. was thereby produced.

From these data we can calculate the following carbon balance of the polymerization process: H₂, CH₄, C₃H₆ and C₃H₈ are produced in negligible amounts; 38% C₂H₄ was recovered unchanged; in addition 6.3% C₂H₆ and 29% (and C₄H₁₀?) with some higher hydrocarbons were formed. The residue on the catalyst amounting to 24% was recoverable as methane by hydrogenation, leaving 3% of the carbon not accounted for in the analysis. This result shows that ethylene certainly polymerizes on a nickel catalyst at room temperatures and that the reactions with hydrogen present must be quite complex, involving hydrogenation, exchange, polymerization and, at sufficiently high temperatures, a decomposition process. It is thus much more complex than the ethane case. The absence of methane and propane indicates the remarkable stability of the C—C bond which does not materially break while these several processes of hydrogenation, exchange and polymerization are freely occurring.

Discussion of Results

As in the case of ethane² the apparent activation energy required to break the C—C bond in propane on the catalyst surface is higher than that required to break the C—H bond. Kinetic studies reveal, as in the case of ethane, that the inhibitory effect of hydrogen is much more marked in the case of C—C bond breaking than in the case of the C—H bond. The exchange reaction is proportional to the -0.76 power of the hydrogen concentration and the decomposition to the -2.6 power. In our present experiments we have studiously avoided experimental conditions in which carbon deposition might occur and the excellent constancy of activity of the catalyst throughout a long series of experiments is additional evidence that such carbon deposition has

not occurred. We therefore can eliminate this possibility as the cause of the high inverse power effect of hydrogen from those discussed in Section II of this series. The form of the kinetic expression in both reactions indicates that the catalyst surface is largely occupied by hydrogen. The bare centers available for activated adsorption of propane should therefore be inversely proportional to some fractional power of the deuterium concentration. The data on the exchange reaction agree with this conclusion and indicate a fraction, -0.76 . The much higher inhibitory effect in the decomposition reaction indicates quite decisively that much larger areas of surface are required for the propane to undergo this reaction than for the exchange process. At least two elementary spaces (in the sense of Langmuir) of a less frequent type than those adequate for exchange are demanded by an exponent of magnitude, -2.6 . It is possible that even more than two elementary spaces are required for the dissociative adsorption which sunders the C—C bond. Whatever the area demanded, the kinetic studies here reported are excellent proof of the theory of active centers specific for a particular reaction even though the reactions studied are, as in this case, two different reactions with the same two gases present in the same concentrations. The range of temperatures in which the reactions could be studied was not sufficiently great for any variation in the dependence on the hydrogen pressure to be revealed. The abnormally high activation energy of the process may, however, as in the case of ethane, be explained as due to the composite effects of reaction temperature and relative surface coverage.

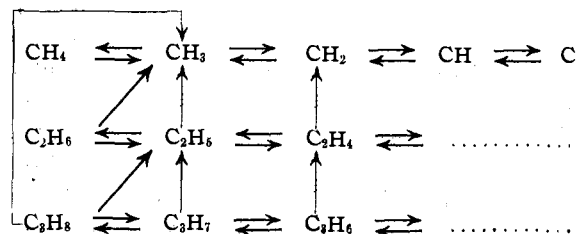
In the case of ethylene and propylene it is to be noted that exchange occurs even on a relatively inactive exchange catalyst such as copper, on which, under the conditions employed, no activation of the C—H or C—C bonds in saturated hydrocarbons occurs. We thus conclude that the presence of the double bond in the olefin markedly weakens the C—H bonds so that exchange occurs prior to hydrogenation, or at least during the hydrogenation process, possibly according to the suggested mechanism of Horiuti and Polanyi.¹⁰

General Discussion

From the data presented in the group of papers of which this is the third, we conclude that, under

(10) Horiuti and Polanyi, *Trans. Faraday Soc.*, **30**, 1171 (1934).

the conditions of our experimental work, the activated adsorption of saturated hydrocarbons is dissociative in type. We illustrate the various possibilities diagrammatically (the hydrogen atoms formed by dissociation being omitted for simplicity) thus



In respect to the positions of equilibria in such a complex system we observe that, with a high partial pressure of hydrogen, the equilibrium is largely on the molecular side and at low hydrogen partial pressure the equilibrium shifts toward carbon. The higher the hydrocarbon the more pronounced the shift toward the carbon side. In

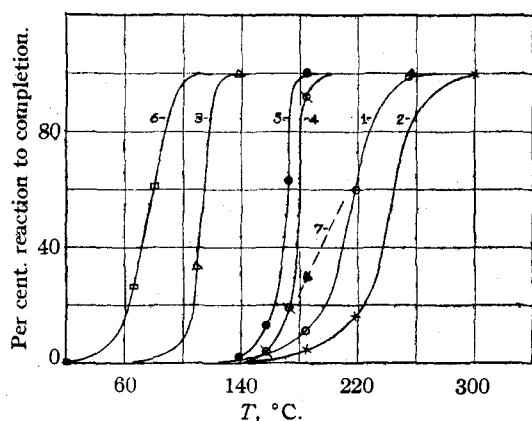


Fig. 3.—

Curve	Reaction	Time, hrs.
1	$\text{CH}_4 + \text{CD}_4 \rightarrow \text{Ex.}$	1
2	$\text{CH}_4 + \text{D}_2 \rightarrow \text{Ex.}$	1
3	$\text{C}_2\text{H}_6 + \text{D}_2 \rightarrow \text{Ex.}$	2.5
4	$\text{C}_2\text{H}_6 + \text{H}_2 \rightarrow 2\text{CH}_4$	1
5	$\text{C}_3\text{H}_8 + 2\text{H}_2 \rightarrow 3\text{CH}_4$	1
6	$\text{C}_3\text{H}_8 + \text{D}_2 \rightarrow \text{Ex.}$	1
7	$\text{CH}_4 + \text{D}_2\text{O} \rightarrow \text{Ex.}$	11

the absence of hydrogen, ethane changes to methane and carbon which are the only thermodynamically stable molecules in a system so constituted.⁴ Below 300°, the equilibrium in the system $\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$ is pronouncedly on the methane side so that if the carbon is in a sufficiently active form it can be converted to methane with hydrogen.⁴

With mixtures of methane and D_2O vapor, owing to the low H-atom concentration on the surface, the dissociative adsorption of methane will proceed markedly toward carbon. The deuteromethane which results will be formed not only from CH_3 fragments but also from CH_2 and CH fragments. We thus explain the abnormal distribution of the deuterium in the deuteromethanes produced by interaction with water³ in contrast to the approximately equilibrium distribution when deuterium is used for the exchange process, methyl groups being the predominant fragments in this case.

The relatively strong adsorption of hydrogen and deuterium in comparison with the hydrocarbons explains the slowness of the $\text{CH}_4 + \text{D}_2$ exchange in comparison with the $\text{CH}_4\text{-CD}_4$ exchange.³ With the higher hydrocarbons, two types of activation of the C-H and C-C bonds are involved. The activation of the former requires less apparent energy than that of the latter, is less adversely affected by hydrogen than is the latter. Our data reveal no evidence of the occurrence of reverse processes such as $2\text{CH}_2 = \text{C}_2\text{H}_4$, occurring from an upper to a lower level in the diagram given above. Under different conditions, as for example in the Fischer process of gasoline synthesis, such processes may be occurring.

We summarize, for comparative purposes in Fig. 3, the velocities of the various reactions we have studied on nickel catalysts. There are variations in the activities of the catalysts used, so that the data are only to be taken as approximate for comparison purposes. They do, however, reveal, the general course of activation as we proceed from methane toward the more complex hydrocarbons.

Summary

1. The exchange reaction between propane and deuterium on a nickel catalyst takes place in a lower temperature range, by $\sim 90^\circ$, than that of the hydrogenation-decomposition to yield ethane and methane.
2. The kinetics of the two processes have been studied. The reactions are inhibited by hydrogen, the exchange to the -0.76 power, the decomposition to the -2.6 power of the hydrogen concentration.
3. Methods for the preparation of propane- d_8 as well as deuteropropanes and deuterioethanes of known C-D content have been described.
4. The availability of the hydrogen in a nickel-

kieselguhr catalyst for exchange reactions has been studied. Adsorbed hydrogen and adsorbed water vapor may be removed by evacuation at 218°. Other hydrogen sources of reproducible availability are held tenaciously in the kieselguhr, probably as bound water. These are difficult to remove even at 400–500°, and exchange with deuterium to increasing extents with increase of temperature.

5. The deuterium-ethylene reactions on nickel

in the range -80 to 65° results in some exchange as well as the addition reaction. A copper catalyst also shows activity in exchange.

6. Ethylene polymerizes to C_4 and higher hydrocarbons at 0° on nickel, but the breaking of the C-C linkage is negligible.

7. A general discussion in terms of the dissociative adsorption of the saturated hydrocarbons has been given.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GREENSBORO COLLEGE]

Aqueous Solubilities of the Isomeric Pentanols

By P. M. GINNINGS AND RHODA BAUM

An important factor in most investigations of the relationship between molecular structure and aqueous solubility of organic compounds is the molecular weights of the compounds studied. In fact its domination frequently tends to obscure the effect of lesser factors. Evidently, limitation of a study to isomers should simplify considerably analysis of the results and for this reason, a study of the aqueous solubilities of the eight isomeric pentanols or amyl alcohols seemed worthwhile. Search of the literature revealed approximate solubilities for many of these isomers but apparently only two have been measured precisely. Butler¹ using an interferometric method measured the solubility of *n*-pentanol (*n*-butylcarbinol) at 25° as 2.208 weight percentage. Kablukov² using the volumetric method of Hill³ determined the value for isobutylcarbinol (isoamyl alcohol) at a number of temperatures. Values for the latter are also given in the "International Critical Tables."⁴

The solubilities of these two compounds were also determined in the present paper as a check upon our experimental work and the results seem to agree within the accuracy of our method.

Results of our determination of the weight percentage solubilities of these eight isomers are given in the table. The difference between the larger weight percentage for a given temperature and isomer and one hundred represents the solubility of water in that particular isomer. Analysis

of the data indicates that the one tertiary isomer is more soluble than any of the three secondary isomers and that these in turn are more soluble than any of the four primary isomers. The solubility increases as the hydroxyl group approaches the center of the molecule (Nos. 1, 5 and 6). If the analysis is limited to either the primary or secondary isomers, it is evident also that the solubility in water increases as the structure of the molecule becomes more compact. However, the most compact primary isomer (No. 4) is not as soluble as the least compact secondary isomer (No. 5). Usually the more soluble the alcohol in water, the more soluble the water is in the alcohol. Of interest also is the fact that as the temperature increases from 20 to 30° , the solubility of all eight isomers decreases.

Experimental

With one exception, the compounds used for the final determinations were prepared by purification of products synthesized by one of the Grignard reactions. *t*-Butylcarbinol was prepared in this Laboratory by the action of *t*-butylmagnesium chloride upon paraformaldehyde with the usual hydrolysis, etc. Dimethylethylcarbinol was prepared by the action of ethylmagnesium bromide upon acetone in the usual Grignard procedure. The other compounds were Eastman best grade of products. The isobutylcarbinol probably was obtained originally as a by-product from a fermentation process and was known to contain some of the active amyl isomer. Approximately seventy-five aqueous extractions, drying with anhydrous potassium carbonate and final fractional distillation over metallic calcium seemed to purify this satisfactorily.

In general, all products from the Grignard syntheses were fractionally distilled with a short column (reflux

(1) Butler, Thompson and MacLennan, *J. Chem. Soc.*, 674 (1933).

(2) Kablukov and Malischeva, *THIS JOURNAL*, 47, 1559 (1925).

(3) Hill, *ibid.*, 45, 1145 (1923).

(4) "International Critical Tables," Vol. 111, p. 388.