

After a varying degree of undercooling, all the naphthenes and aromatics examined could be brought to crystallization; transition points were observed with cyclopentane and cyclohexane.

In addition to published data, we also studied a number of freezing point diagrams of binary hydrocarbon mixtures.

As a rule there is a eutectic point and the freezing point curves of the components conform

to the formula for the ideal freezing point curve.

There is probably an interrupted series of mixed crystals in the *n*-octane-*n*-nonane system and a continuous series of mixed crystals in the 2,2,3-trimethylbutane-2,2,3,3-tetramethylbutane system.

Most of the binary iso-paraffin mixtures produced glass formation.

AMSTERDAM, NETHERLANDS RECEIVED AUGUST 10, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, THE HEBREW UNIVERSITY]

## The Catalytic Interaction of Ethylene and Heavy Hydrogen on Platinum

BY A. FARKAS AND L. FARKAS

The catalytic interaction of ethylene and hydrogen can involve a number of reactions, such as hydrogenation, exchange of hydrogen atoms,<sup>1</sup> polymerization, and formation of methane and other hydrocarbons.<sup>2</sup> The present paper deals with the first two of these reactions. It contains the study of the exchange reaction and includes some contribution on the mechanism of the hydrogenation obtained by using para-hydrogen and heavy hydrogen as research tools.

The experimental method used was the same as in the previous communications.<sup>3</sup> A platinumized platinum foil was used as catalyst. The activity of the catalyst was fairly constant even when the catalyst was heated to elevated temperatures, if care was taken to avoid poisoning by grease or mercury. A freshly prepared catalyst was the most active and its activity decreased somewhat in the course of a few days. In spite of this variation the experiments are comparable since it was always ascertained that the activity should not change when one parameter was being varied during one series of runs. The same numbers of the experiments, *e. g.*, 37a, 37b, etc., will refer to the catalyst being in the same state of activity, which was usually constant during a day.

The reaction vessel had a volume of 60 cc. and was kept in a Dewar vessel at the required temperature by means of an ice- or oil-bath heated electrically. The hydrogenation was followed manometrically and the amount of exchange es-

timated by determining the change in the D-content of the hydrogen by the micro-thermal conductivity method.<sup>4</sup> This was possible since the D-content of the hydrogen was not changed when left in contact with the catalyst in the absence of ethylene, showing that the catalyst did not absorb or retain any appreciable amount of hydrogen. Since the amount of gas extracted from the reaction vessel was very small, several measurements could be performed in the same run without changing the pressure in the reaction vessel appreciably.

The ethane and ethylene were separated from the hydrogen by passing the gas mixture through a trap cooled with liquid air boiling at 5 to 10 mm. pressure (53°A.).

The progress of the hydrogenation is represented in Fig. 1 at 25° for different hydrogen and ethylene mixtures. It will be recognized that the rate of reaction decreases with increasing ethylene pressure and increases with the hydrogen pressure. The progress of the reaction can be represented approximately by

$$P = P_0 \exp. (-kt) \quad (1)$$

$P$  and  $P_0$  designating the pressure of the reactant not in excess at the time  $t$  and  $t = 0$ , respectively.

The temperature dependence of the hydrogenation is shown in Fig. 2 for mixtures of 40 mm.  $H_2$  + 20 mm.  $C_2H_4$  at 0-78°,  $\log P/P_0$  for ethylene being plotted against time. In this region and up to about 150° the temperature dependence of the hydrogenation corresponds to the Arrhenius equation with an energy of activation of 10 kcal. as is shown by curve A in Fig. 3, in

(1) Farkas, Farkas and Rideal, *Proc. Roy. Soc. (London)*, **A146**, 630 (1934).

(2) Morikawa, Trenner and Taylor, *THIS JOURNAL*, **59**, 1103 (1937).

(3) (a) A. and L. Farkas, *Trans. Faraday Soc.*, **33**, 678 (1937); (b) A. and L. Farkas, *ibid.*, **33**, 827 (1937).

(4) A. and L. Farkas, *Proc. Roy. Soc. (London)*, **A144**, 467 (1934).

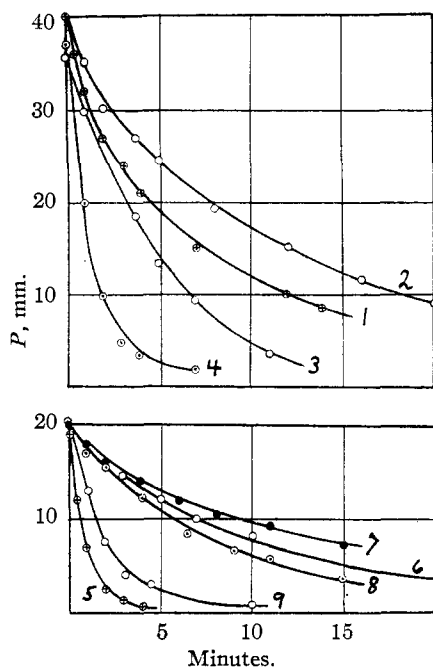


Fig. 1.—1, 40 mm.  $H_2$  + 73 mm.  $C_2H_4$ ; 2, 40 mm.  $H_2$  + 111 mm.  $C_2H_4$ ; 3, 39.5 mm.  $H_2$  + 35.5 mm.  $C_2H_4$ ; 4, 67 mm.  $H_2$  + 37 mm.  $C_2H_4$ ; 5, 60 mm.  $H_2$  + 19 mm.  $C_2H_4$ ; 6, 20 mm.  $H_2$  + 71 mm.  $C_2H_4$ ; 7, 20 mm.  $H_2$  + 40 mm.  $C_2H_4$ ; 8, 20.5 mm.  $H_2$  + 21.5 mm.  $C_2H_4$ ; 9, 50 mm.  $H_2$  + 20 mm.  $C_2H_4$ . The runs were carried out in this order.

which the logarithms of the half-life times of the hydrogenation (expts. 28a to 28e, Fig. 2) are plotted against the reciprocal of absolute temperature. The line  $A_2$  refers to the experiments (Nos. 27a to 27f) with the catalyst in a less active state. It will be recognized that lines  $A_1$  and

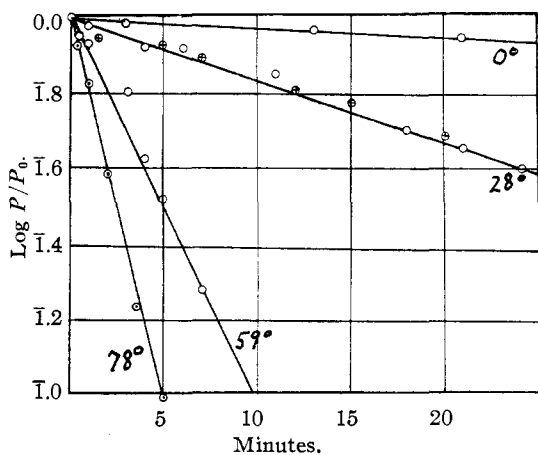


Fig. 2.—The runs were carried out in the following order: 28° (points marked by 0), 78°, 59°, 28° (points marked by ⊕) and 0°.

$A_2$  are parallel, indicating the same energy of activation in the low temperature region in both series. At higher temperatures the rate of hydrogenation decreases. This observation is in agreement with the results of earlier investigators.<sup>5-7</sup>

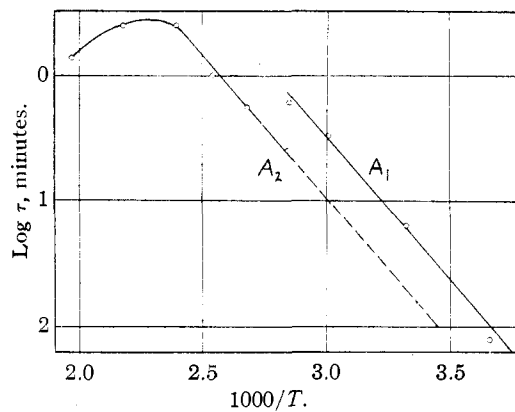


Fig. 3.

#### The Rate of Hydrogenation with $H_2$ and $D_2$ and the Rate of the ortho-para-Conversion.—

The rates of hydrogenation with  $H_2$  and  $D_2$  at 25° are shown on Fig. 4 in two typical examples. Curve (a) refers to a mixture of 28 mm.  $H_2$  + 53 mm.  $C_2H_4$  and curve (b) to a mixture of 29.5 mm.  $D_2$  + 52.5 mm.  $C_2H_4$ . The hydrogenation with

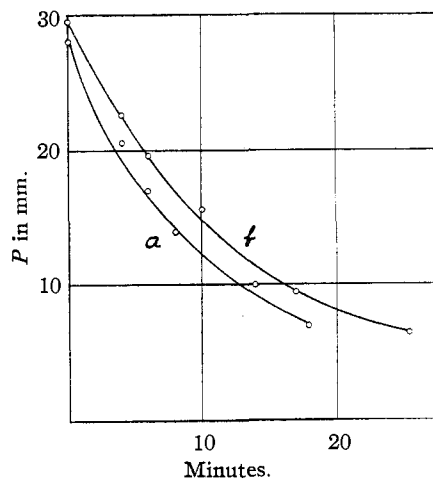


Fig. 4.—a, 28 mm.  $H_2$  + 53 mm.  $C_2H_4$ ; b, 29.5 mm.  $D_2$  + 52.5 mm.  $C_2H_4$ .

$H_2$  proceeds 1.2 times more quickly than that with  $D_2$ . The ratio is somewhat smaller than the one measured by other investigators who worked with other catalysts and under different pressures.<sup>8,9</sup>

- (5) Rideal, *J. Chem. Soc.*, 121, 309 (1922).
- (6) Zur Strassen, *Z. physik. Chem.*, **A169**, 81 (1934).
- (7) Tuchsolski and Rideal, *J. Chem. Soc.*, 1071 (1935).
- (8) Klar, *Z. physik. Chem.*, **B27**, 317 (1934).
- (9) Pease and Wheeler, *THIS JOURNAL*, **57**, 1149 (1935).

In order to obtain some information about the state and concentration of the hydrogen in the surface of the catalyst<sup>3,10</sup> the rate of hydrogenation was compared with: (a) the conversion of para-hydrogen in the absence of C<sub>2</sub>H<sub>4</sub>; (b) the conversion of orthodeuterium in the absence of C<sub>2</sub>H<sub>4</sub>; (c) the reaction of H<sub>2</sub> + D<sub>2</sub>  $\rightleftharpoons$  2HD in the absence of C<sub>2</sub>H<sub>4</sub>; (d) the conversion of para-hydrogen in the presence of C<sub>2</sub>H<sub>4</sub>. The hydrogenation was compared with reaction (d) by measuring the decrease of pressure and the concentration of para-hydrogen in a mixture of ethylene and para-hydrogen simultaneously.

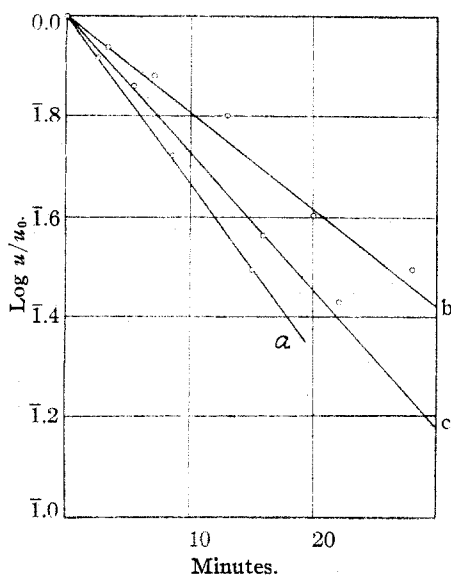
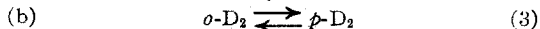
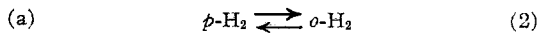


Fig. 5.—a,  $p\text{-H}_2 \rightleftharpoons o\text{-H}_2$ ; b,  $o\text{-D}_2 \rightleftharpoons p\text{-D}_2$ ; c,  $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$ .

On Fig. 5 the reactions (a), (b) and (c) are compared with each other at 18 mm. pressure and 26° (expts. 30c, d and g) the logarithm of the "distance" from equilibrium ( $\log u/u_0$ ) being plotted against time. It will be recognized that the reactions



proceed with rates in the ratio 1.84 : 1 : 1.25 indicating that all three reactions involve the same mechanism. At -12° on a catalyst of slightly different activity the ratio of the rates of reactions (2) and (3) was found to be 1.73. The dependence of the conversion of para-hydrogen on temperature corresponds to an energy of activation of 10-11 kcal., *i. e.*, to the same value as that

(10) Farkas, *Trans. Faraday Soc.*, **32**, 416, 922 (1936).

of the hydrogenation in the low temperature region. Through the presence of ethylene the rate of para-conversion is reduced considerably, in agreement with earlier observations on a nickel catalyst<sup>1</sup> as shown by Table I which summarizes also the relative rates of the conversion of para-hydrogen and hydrogenation in different mixtures. The quantities  $\tau_c$  and  $\tau_h$  in columns 5 and 6 are the half-life times for the conversion and for the hydrogenation, respectively.

TABLE I

No.	Temp., °C.	C <sub>2</sub> H <sub>4</sub> , mm.	<i>p</i> -H <sub>2</sub> , mm.	$\tau_c$ for conversion in minutes	$\tau_h$ for hydrogenation in minutes
31a	25	40	21	80	80
31b	25	..	21	14	..
31c	0	..	21	72	..
37f	0	..	40	6	..
37h	0	19	40	50	13
29a	23	..	15	7.7	..
29c	24	42.5	17.5	45	45
30h	27	..	12.5	15.8	..
30j	27	36.5	12.5	45	45

The absolute rate of the para-conversion in the absence of ethylene, *i. e.*, the number of molecules converted, is about five times larger than the absolute rate of hydrogenation, *i. e.*, the number of molecules hydrogenated. A similar ratio was found for very much less active catalysts. If ethylene is in excess the hydrogenation and the conversion of para-hydrogen in the presence of ethylene proceed approximately with the same speed. If, however, hydrogen is in excess, the hydrogenation proceeds relatively much faster than the conversion of para-hydrogen in the presence of ethylene (*cf.* discussion, p. 25). Consequently the ethylene is used up before all para-hydrogen could be converted. A fast conversion sets in as soon as the ethylene disappears.<sup>1</sup>

The exchange reaction has been compared with the hydrogenation by measuring the decrease of pressure and the change of D-content in a mixture of deuterium and ethylene simultaneously.

First of all it was established that: (a) the D-content of deuterium did not change if it was in contact with the catalyst in the absence of ethylene up to a temperature of 230° within half an hour; (b) there was no exchange between ethane and deuterium; and (c) under the present experimental conditions the hydrogenation led directly to ethane and no polymerization or formation of methane could be detected.

The exchange reaction proceeded only at elevated temperature when the hydrogenation was

already very fast. For this reason, the end-point of the exchange reaction was measured by determining the final D-content of the residual hydrogen in a mixture containing excess of deuterium (mostly 40 mm. D<sub>2</sub> + 20 mm. C<sub>2</sub>H<sub>4</sub>) after the hydrogenation reaction had been completed and all ethylene had been used up. Table II summarizes the results obtained.

TABLE II

No.	Temp., °C.	D <sub>2</sub> in mm.	C <sub>2</sub> H <sub>4</sub> in mm.	%D in equilib- rium (D <sub>theor.</sub> )	Final D- content in % (D <sub>exptl.</sub> )	% exchange $r = \frac{100 - D_{exptl.}}{100 - D_{theor.}} \times 100$
37b	25	40	21	37	99	1.5
25e	54	40	20	40	95	8
27a	79	40	20.5	41	80	34
27b	100	39.5	21	40	75	42
27c	120	40	21	41	63	63
27e	146	40	21	42	59	70
27d	187	40	21	43	51	86
27f	235	39.5	22	44	48	93

The data in column 5 were calculated assuming that the distribution of protium and deuterium between hydrogen and ethylene is the same as between hydrogen and water,<sup>11</sup> since, according to Wirtz,<sup>12</sup> the distribution coefficient for hydrogen and deuterium in the systems water-aliphatic C-H bonds and water-aromatic C-H bonds is about unity.

This table indicates that with increasing temperature the speed of the exchange increases rapidly, and at about 230° the equilibrium is nearly completely established.

The dependence of the exchange on the pressure at 100° is summarized in Table III. At lower pressures the exchange comes nearer to completion.

TABLE III

No.	D <sub>2</sub> mm.	C <sub>2</sub> H <sub>4</sub> mm.	%D in equilibrium	Final D-content, %	r % exchange
23c	20	10	42	65	60
23b	39.5	21.5	39	75	41
23d	78	37	43	80	35

## Discussion

**A. The hydrogenation** may involve the activation of hydrogen or/and that of the ethylene. Concerning the activation of hydrogen we can obtain useful information from the experiments on the conversion and interchange reactions of the hydrogen modifications. In a number of previous papers,<sup>13</sup> it was shown that the rate of

the catalytic conversion of para-hydrogen measures directly the rate of dissociation of the hydrogen molecules on the surface of the catalyst. The present experiments on the relative speeds of the reactions  $p\text{-H}_2 \rightleftharpoons o\text{-H}_2$ ,  $o\text{-D}_2 \rightleftharpoons p\text{-D}_2$  and  $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$  add further evidence for the mechanism of these reactions and exclude the possibility of the migration of atoms (and not the dissociation of molecules) on the surface of the catalyst being the rate determining step for the conversion or the interchange reactions.

If the migration of the atoms be the rate determining step one would expect the interconversion of the ortho- and para-modifications to proceed faster than the reaction  $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$  since the reunion of two atoms formed from the same molecule should lead to ortho-para-conversion but not to formation of HD. The reaction  $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$  can occur only if the H or D atoms formed primarily migrate to a neighboring atom. In fact, it is found that the rate of the reaction  $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$  lies between that of (2) and (3). The slight difference in the rates of reactions (2), (3) and (4) suggests that the difference in the energies of activation of these reactions cannot be larger than 2-300 cal. This indicates that the difference in the zero point energies of the initial state and of the intermediate state involved in these reactions cancel reciprocally. This is similar to the state of affairs in the thermal interchange reactions in the gaseous state.<sup>14,15</sup>

The following facts emerge from the comparison of the rate of the para-conversion in the absence of ethylene with that of the hydrogenation:

The absolute rates of both reactions are in the same ratio on catalysts of different activity.

The ratios of the hydrogenation with hydrogen and deuterium are about the same as that of the ortho-para-conversion for hydrogen and deuterium.

The energy of activation is 10-11 kcal. for both reactions.

These facts suggest that the rate-determining step is the same in both reactions, *i. e.*, both the ortho-para-conversion and the hydrogenation are controlled by the dissociation of hydrogen.<sup>16</sup>

On the basis of the present experiments it is

(11) A. and L. Farkas, *Trans. Faraday Soc.*, **30**, 1017 (1934).

(12) Wirtz, *Z. Elektrochem.*, **43**, 662 (1937).

(13) Farkas, "Ortho-Hydrogen, Para-Hydrogen and Heavy Hydrogen," The Cambridge University Press, Cambridge, England, 1935.

(14) A. and L. Farkas, *Proc. Roy. Soc. (London)*, **A52**, 124 (1935).

(15) Farkas and Wigner, *Trans. Faraday Soc.*, **32**, 1 (1936).

(16) This state of affairs is similar to that in the diffusion of hydrogen through palladium [Farkas, *Trans. Faraday Soc.*, **32**, 1667 (1937)].

even possible to describe the rate determining step quantitatively as follows:

The absolute rate of para-hydrogen conversion in the absence of ethylene is the maximum rate of dissociation of molecules under the given pressure and temperature.

In the presence of ethylene, part of the hydrogen adsorbed on the catalyst is replaced by ethylene and a number of atoms formed will be added to ethylene molecules before they have any chance to recombine to molecules. The number of hydrogen atoms added to ethylene is measured by the hydrogenation. The number of recombinations is measured by the para-conversion in the presence of ethylene.

The absolute rate is expressed by  $Vk[C] = (\ln 2) V [C]/\tau$  (provided the reaction is of the first order),  $k$  being the velocity constant,  $\tau$  the half life time,  $[C]$  the concentration and  $V$  the volume of the reaction vessel. Thus one finds from Table I the following figures.

TABLE IV

No.	Dissociated per sec. in the absence of ethylene	In the presence of ethylene Recombined per sec.	Added per sec.
37f-h	$1.6 \times 10^{17}$	$2.0 \times 10^{16}$	$3.6 \times 10^{16}$
30h-j	$1.8 \times 10^{16}$	$6.0 \times 10^{15}$	$6.0 \times 10^{15}$

It will be recognized that at least as many molecules are added to ethylene as are dissociated and reunited at the same time. Since in the addition of hydrogen to ethylene the activation consists in the dissociation of the hydrogen molecules, the sum of the added molecules and converted molecules represents the total number of hydrogen molecules dissociated in the presence of ethylene. This number—as shown by Table IV—is smaller than the number of molecules dissociated (converted) in the absence of ethylene. This indicates that ethylene occupies a large area of the catalyst.

In a previous paper,<sup>3a</sup> it was shown that benzene and hydrogen do not occupy the same places on a platinum catalyst. In fact, only very few places are available for the benzene molecules, and it was suggested that this was due to geometrical reasons. It is very probable also that the ethylene molecules cannot occupy all places which are active in dissociating hydrogen molecules. In contrast to the state of affairs in the catalytic interaction of benzene and hydrogen, the number of places not available for ethylene is small compared with the number of those occupied, as is shown by the figures in Table IV. The number

of places not available for ethylene is proportional to the rate of para-conversion in the presence of ethylene in large excess.

The data of Table IV can be regarded as evidence for the same mechanism being involved in the hydrogenation of ethylene as suggested in a previous paper:<sup>3a</sup> two atoms of hydrogen are added simultaneously and not subsequently. These two atoms are formed from the same molecule through dissociation. This mechanism is valid at low temperatures at which the hydrogenation has been compared with the conversion of para-hydrogen, but not necessarily at high temperatures when the hydrogenation might involve a successive addition of two hydrogen atoms.

Accordingly, we have to make the following picture of the catalytic hydrogenation of ethylene. In the absence of ethylene the rate of the catalytic dissociation of the hydrogen molecules and the rate of the subsequent recombination of the atoms is large as measured by the rate of the para-conversion. In the presence of ethylene, particularly when in excess, most of the hydrogen is displaced. The rate of the recombination of the hydrogen atoms is reduced for this reason, and, furthermore, through the addition of the addition of the atoms of the ethylene molecules.

This picture readily explains the dependence of the rate of hydrogenation on the pressure of hydrogen and of ethylene. If the pressure of ethylene is increased, more and more hydrogen is displaced, and consequently there is less chance for hydrogenation. With increasing pressure of hydrogen, however, the concentration of hydrogen in the adsorption layer increases and therefore the rate of hydrogenation increases also. The upper limit for the order of reaction with regard to the hydrogen pressure should be unity. In fact it is found that this order is higher. At present we have no other explanation to offer than that the temperature of the catalyst might have been slightly increased by the heat evolved during the quick reaction taking place.

The temperature dependence of the hydrogenation is due to the activation of hydrogen. This is true up to a temperature at which the hydrogenation begins to decrease. The negative temperature coefficient of the hydrogenation at higher temperatures is generally attributed to the desorption of ethylene and hydrogen. The occurrence of the exchange reaction suggests an-

other explanation which will be dealt with presently.

**B. The Exchange Reaction.**—The data of Table II show that with increasing temperature the rate of the exchange increases. This can only happen if the temperature coefficient of the exchange is larger than that of the hydrogenation, since the exchange reaction cannot proceed further as soon as all the ethylene is used up by the hydrogenation reaction.

It is evident that if the ratio of the velocities for exchange and hydrogenation is zero or infinite, the percentage of exchange ( $r$ ) listed in column 7 of Table II will be 0 or 100, respectively. For any intermediate case one can use the approximation Exchange/Hydrogenation =  $r/(100-r)$ . The ratios calculated in such a way are listed in Table V.

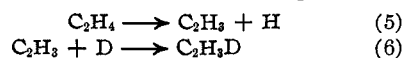
TABLE V

°C.	Ratio Exchange/hydrogenation
25	0.02
54	.08
79	.5
100	.7
120	1.7
146	2.3
187	6.1
235	13.3

The dependence of the rate of exchange reaction on temperature is represented graphically on Fig. 6 (curve a), the rates being obtained by multiplying the rate of hydrogenation (curve b) by the ratios of Table V. The points thus calculated, except those at higher temperatures, lie fairly well on a straight line. The discrepancy at higher temperatures is due to the fact that even a small error in the determination of the final D-content or in the calculation of the D-content in equilibrium can cause a great change in the values of the ratios of Table V.

The slope of line (a) corresponds to an activation energy of 22 kcal., which is considerably higher than that of the hydrogenation reaction.

It was suggested<sup>1</sup> that the mechanism of the exchange reaction involves the steps



The present results indicate that reaction (5) is the rate determining step and that the activation energy of 20 kcal. is associated with this step.

A glance at Fig. 6 shows that the well-known decline of the hydrogenation with increasing temperature sets in as soon as the rate of the exchange

reaction becomes comparable with that of the hydrogenation. In the light of the present experiments the negative temperature coefficient of the hydrogenation is directly connected with the exchange reaction and not to be attributed to the decreasing density of the ethylene in the adsorption layer. This is the more so since the hydrogenation reaction happens to have a rather high energy of activation of 10 kcal.

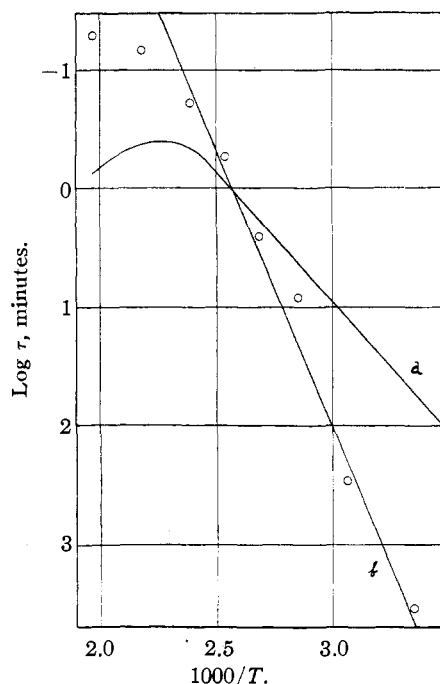
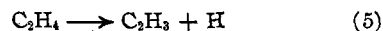


Fig. 6.—a, Hydrogenation; b, exchange.

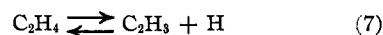
With increasing temperature the catalytic exchange reaction increases since the rate determining step



has a strong positive temperature coefficient. It is very probable that the velocity constant of the reverse reaction



is not much dependent on temperature and therefore the equilibrium



on the surface of the catalyst is more and more shifted toward the right-hand side as the temperature increases. Consequently, the rate of hydrogenation will decrease since the partially decomposed ethylene molecules are not available for adding hydrogen and forming ethane. This is the cause for the decline of the hydrogenation at elevated temperatures and not the change of the concentration in the adsorption layer.

The dependence of the rate of exchange on the pressure (Table III) is explained readily with reaction (5) being the rate determining step. In the pressure range of the present experiments the concentration of ethylene in the adsorption layer does not increase proportionally to the pressure. Since the rate determining step is the dissociation of ethylene, the relative rate of exchange will decrease with increasing pressure.

### Summary

The interaction of heavy hydrogen and ethylene has been investigated on platinized platinum foil at pressures of 10–100 mm. in the temperature range 0–236°. It is shown that two reactions occur: hydrogenation according to  $C_2H_4 + D_2 = C_2H_4D_2$  and exchange according to  $C_2H_4 + D_2 = C_2H_3D + HD$ . In the temperature range 0–150° the hydrogenation has a temperature coefficient higher than unity corresponding to an energy of activation of 10 kcal. Above 150°

the temperature coefficient is smaller than unity. A comparison of the hydrogenation with the ortho-para-conversion of  $H_2$  and  $D_2$  and with the reaction  $H_2 + D_2 \rightleftharpoons 2HD$  shows that in the lower temperature range the rate determining step is the activation of hydrogen molecules which involves the loosening of the bond between their two atoms.

The temperature coefficient of the exchange reaction is larger than that of the hydrogenation and corresponds to an energy of activation of 22 kcal. The rate-determining step of the exchange reaction is the reaction  $C_2H_4 \rightarrow C_2H_3 + H$ . It is shown that the temperature coefficient of the hydrogenation above 150° is not due, as was hitherto assumed, to the desorption of ethylene, but to the shifting of the equilibrium  $C_2H_4 \rightleftharpoons C_2H_3 + H$  toward the right-hand side owing to the high temperature coefficient of the rate determining step.

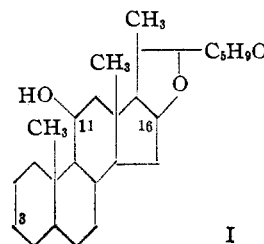
JERUSALEM, PALESTINE RECEIVED SEPTEMBER 22, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## Sarsasapogenin. I. An Investigation of the Side Chain

BY LOUIS F. FIESER AND ROBERT P. JACOBSEN<sup>1</sup>

This investigation of the comparatively readily available sapogenin from sarsaparilla root was undertaken partly in the hope of gaining a further insight into the nature of the terminal portion of the side chain characteristic of the steroid sapogenins and partly with the idea that it might be possible to degrade the compound into physiologically active substances of the sex hormone type. At the time the work was undertaken Jacobs and Simpson<sup>2</sup> had established the principal outlines of the structure of the aglycone and the tentative formula I,<sup>3</sup> or the alternate formula<sup>2d</sup> with the oxidic bridge extending to C<sub>15</sub> instead of C<sub>16</sub>, was uncertain only with respect to the point just mentioned and the location of the nuclear secondary hydroxyl group. Askew, Farmer and Kon<sup>4</sup> subsequently reported surface film measurements which could not be reconciled with the view<sup>2c</sup> that



the hydroxyl group is situated at C<sub>11</sub> in ring C, and from their results, and from certain other inferences, they concluded that the group in question probably is located either at the characteristic sterol position (C<sub>3</sub>) or at C<sub>2</sub>. This gave further impetus to the degradative work which we had planned.

Our first line of attack was suggested by the observation of Jacobs and Simpson<sup>2a</sup> that on treatment with hydrochloric and acetic acids sarsasapogenin yields a volatile unsaturated ketone of the formula C<sub>8</sub>H<sub>14</sub>O<sub>3</sub>. This ready elimination of the entire side chain in one step seemed to offer a promising route to a C<sub>19</sub>-compound having a steroid ring system, but we were disappointed in

(1) Du Pont Research Fellow.

(2) (a) Jacobs and Simpson, *J. Biol. Chem.*, **105**, 501 (1934); (b) *This Journal*, **56**, 1424 (1934); (c) Simpson and Jacobs, *J. Biol. Chem.*, **109**, 573 (1935); (d) *Ibid.*, **110**, 565 (1935).

(3) Fieser, "Natural Products Related to Phenanthrene," 2d edition, Reinhold Publishing Corp., New York, 1937, pp. 336–337.

(4) Askew, Farmer and Kon, *J. Chem. Soc.*, 1399 (1936).