403. *The Reaction of Hydrogen and Deuterium with Ethylene at a Nickel Surface.*

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Although an exchange reaction (A. and L. Farkas and Rideal, *Proc. Roy. Soc.*, 1934, *A*, **146**, 630; Melville, this vol., p. 803) readily takes place between hydrogen-containing unsaturated organic compounds and deuterium at catalytic surfaces, the mechanism of the actual process of hydrogenation is not yet elucidated. It is known from the work of Rideal (J., 1922, **121**, 309), zur Strassen (*Z. physikal. Chem.*, 1934, *A*, **169**, 81), and Maxted and Moon (this vol., p. 1190) that the temperature coefficient at low temperatures undergoes a reversal in sign at higher temperatures.

It has been suggested that the reaction velocities below and above the inversion temperature are given by

$$k = ae^{-(E - Q_{H_2})/RT} \text{ and } k = ae^{-(E - Q_{H_2} - Q_{C_2H_4})/RT}$$

respectively, where E, Q_{H_2}, and $Q_{C_2H_4}$ denote respectively the energy of activation and the heats of adsorption of the reactants, *i.e.*, at higher temperatures the adsorption of the ethylene becomes less and thus the amount adsorbed is determined by its energy of desorption and the temperature of the catalyst. Heats of adsorption of ethylene and other organic compounds have indeed been calculated on these premises.

It was thought that some further light might be thrown upon the mechanism, especially as to whether hydrogen or ethylene controlled the rate of hydrogenation above and below the inversion temperature, by investigating the addition reaction with both hydrogen and deuterium under strictly comparable conditions.

EXPERIMENTAL.

The reaction system in its final form, constructed throughout of soda glass, is shown in Fig. 1. The reaction vessel V, of 150 c.c. capacity, contained a 25-cm., 0·2 mm.-diameter, nickel-filament spot welded to alloy leads, and was connected as shown; M_1 and M_2 were mercury traps. The filament was rendered catalytically active by superficial oxidation in air at 600°, followed by reduction in hydrogen at 330°. Loss in activity after prolonged use was restored by heating to 200° in hydrogen or deuterium at low pressures (*ca.* 0·1 mm.). Temperature was measured by a determination of the electrical resistance of the wire which served as one arm of a Wheatstone bridge. The reaction vessel was maintained at the required temperature (constant to ± 0·5°) by an electric furnace or by suitable constant-temperature baths. Hydrogen was purified by passage over hot copper coated with palladium, through charcoal cooled in liquid air, and finally by diffusion through a palladium tube. Deuterium, prepared by decomposition of 96% deuterium oxide on a hot tungsten filament, was purified in a similar manner to the hydrogen. Cylinder ethylene was purified by repeated fractionation. The gases were stored over sodium, and introduced into the reaction system through the taps T_1, T_2, and T_3, the mercury trap M_2 (immersed in solid carbon dioxide–acetone), and finally over a piece of gold foil. Before every experiment, the system was thoroughly evacuated, and the reaction vessel and the connecting tubes were heated with a semi-luminous gas flame. The gas pressure was measured to ± 0·025 mm. with a Bourdon glass-spring gauge of *ca.* 25 c.c. capacity.

FIG. 1

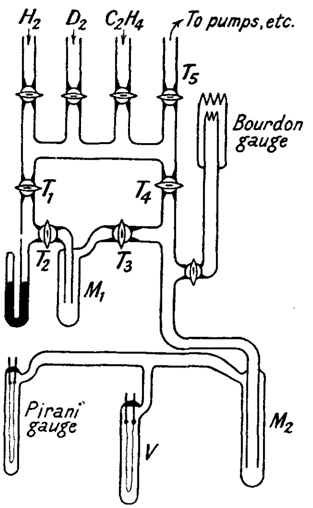
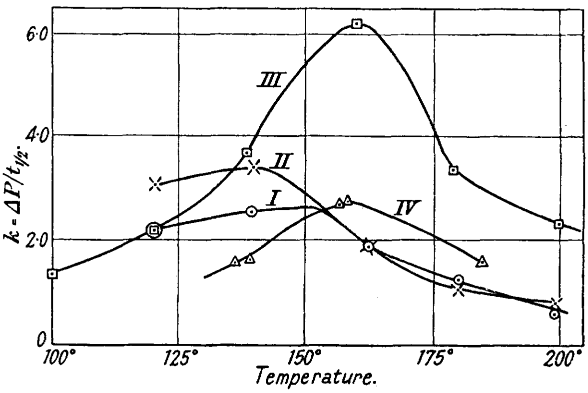


FIG. 2.



This arrangement was only adopted after several different designs had been tested, for, in allowing a mixture of gases of different molecular weights to flow from one vessel to another, there is always a separation of the two gases; the theoretical equation for the maximum separation possible in a system where the mean free path is large compared with the diameter is given by Rayleigh's formula $(H_1/H_2)/(X_1/X_2)^s = (P_0/P)^{s-1}$, where H_1, X_1, P_0 refer to the initial and H_2, X_2, and P to the final values of the composition and pressure, and s for hydrogen and ethylene is $\sqrt{28/2} = 3{\cdot}8$. If, on the other hand, one gas is admitted after the other at high temperatures, an appreciable amount of reaction may take place during the admission of the second gas, unless this operation is performed quickly, and correct velocity curves are difficult to obtain.

Results.

At – 23° (the m. p. of carbon tetrachloride), the reaction velocity was extremely slow, only 6% conversion occurring in 30 minutes. At 0° and higher temperatures, the reaction proceeded at a steady rate and was almost of zero order, as is shown by the following data, where *t* is in minutes and *P* in mm. :

Nickel I.						*Nickel* II.					
Temp. 0°; vol. of system, 205 c.c.						Temp. 17°.					
H_2, 8 mm.; C_2H_4, 5·2 mm.			D_2, 8 mm.; C_2H_4, 4·98 mm.			H_2, 2·1 mm.; C_2H_4, 1·37 mm.			D_2, 2·1 mm.; C_2H_4, 1·31 mm.		
t.	*P*.	$\Delta P/t$.	*t*.	*P*.	$\Delta P/t$.	*t*.	*P*.	$\Delta P/t$.	*t*.	*P*.	$\Delta P/t$.
2	1·05	0·52	2	0·65	0·32	3	0·21	0·070	3	0·13	0·043
3	1·37	0·46	4	1·08	0·27	7	0·50	0·071	6	0·26	0·043
5	2·10	0·40	6	1·60	0·27	9	0·71	0·079	9	0·44	0·049
8	2·95	0·37	9	2·39	0·27	12	0·92	0·075	12	0·58	0·048
10	3·00	0·35	12	2·85	0·24	15	1·13	0·075	15	0·74	0·049
13	4·42	0·34	18	3·28	0·22	17	1·24	0·073	18	0·84	0·047
			20	4·05	0·21	19	1·37	0·072	21	0·92	0·044
			22	4·53	0·21				24	1·07	0·045
									29	1·31	0·044

In the determination of the temperature coefficient of the reaction, carried out over an extensive range of temperatures, it was necessary to perform experiments alternately with hydrogen and deuterium, and in each case the nickel wire was rendered uniformly active by heating to 200° in the appropriate gas before evacuation and subsequent admission of the reacting gases.

Apart from a small relative increase in the velocity of the reaction initially, where errors caused by inaccuracy in the time of admission and by hydrogen or deuterium occluded in the wire are at a maximum, the curves obtained at any one pressure of gas, especially at low pressures, approximate very closely throughout to zero-order reactions, and the calculations based on the temperature coefficient in this paper utilise a zero-order equation.

The results obtained from the equation $k = \Delta P/t_{\frac{1}{2}}$, where $t_{\frac{1}{2}}$ is the half life of the reaction and ΔP the total pressure decrease, together with the ratios of the velocity constants for hydrogen and deuterium, are given in the following table, and the results for one nickel wire (IV) are shown in Fig. 2, Curves I and II.

	Nickel I.		Nickel IV.						
$C_2H_4+H_2(D_2)$, mm.	5+8	5+8	3+5	3+5	5+5	3+5	5+5	3+5	3+5
Temp.	0°	17°	120°	139°	139°	165°	168°	180°	198°
$k_H = \Delta P/t_{\frac{1}{2}}$	0·40	0·58	3·1	3·36	2·80	1·90	1·84	1·01	0·81
$k_D = \Delta P/t_{\frac{1}{2}}$	0·24	0·38	2·25	2·54	1·92	1·84	1·83	1·34	0·54?
k_H/k_D	1·66	1·52	1·38	1·32	1·46	1·03	1·01	0·75	1·5?

From these experiments it would appear that the reaction of ethylene with deuterium has a maximum velocity between 139° and 165°. This result was confirmed by two series of experiments (carried out with deuterium only). In the first series, the partial pressures of ethylene and deuterium were 3 mm. and 5 mm. respectively; in the second, both gases were at an equal partial pressure of 5 mm. The results are shown in the following tables and in Fig. 2, Curves III and IV. Hence, we find that the maximum velocity of the reaction between ethylene and deuterium is obtained at 160°.

3 mm. C_2H_4 + 5 mm. D_2.

Temp.	100·5°	120°	138·5°	159·5°	179·5°	200°
$k_D = \Delta P/t_{\frac{1}{2}}$	1·45	2·25	3·76	6·23	2·90	2·35

5 mm. C_2H_4 + 5 mm. D_2.

Temp.	136°	162°	163°	139°	179°
k_D	1·63	2·50	2·52	1·66	2·1

DISCUSSION.

The hydrogenation of ethylene proceeds more rapidly with light than with heavy hydrogen below the temperature at which the inversion of the temperature coefficient takes place.

The difference in the energies of activation for the reaction velocities of the two hydrogen isotopes between 0° and 20°, calculated by means of the van 't Hoff isochore $\log k_2/k_1 = \Delta E(1/T_2 - 1/T_1)/R$, is $\Delta E = 0{\cdot}79$ kg.-cal. At higher temperatures, up to 140°, ΔE is somewhat less, *viz.*, 0·5 kg.-cal., and above 140° the two reactions proceed with nearly identical speeds. Pease and Wheeler (*J. Amer. Chem. Soc.*, 1935, **57**, 1149) obtained for the hydrogenation of ethylene on a copper catalyst the following values for k_H/k_D : at 0°, 1·59; at 184°, 1·34; at 306°, 1·04. Similar values were obtained by Klar (*Z. physikal. Chem.*, 1934, *B*, **27**, 319), using an iron catalyst.

We infer that zur Strassen's suggested mechanism by which the temperature coefficient undergoes a change in sign cannot be correct, for this is dependent, according to the hypothesis, on the evaporation of the ethylene, leaving the hydrogen mechanism unchanged.

Although no complete formulation can be advanced at this stage, yet certain definite conclusions may be drawn from these experiments which throw some light on the actual mechanism. It is evident that two separate reactions control the process, one operative at low temperatures, the other at high. The value of the difference in the energies of activation for hydrogen and deuterium at low temperatures, $\Delta E = 0{\cdot}79$ kg.-cal., is in close agreement with the value of $\Delta E = 0{\cdot}7$ kg.-cal. calculated by Eyring and Sherman (*J. Chem. Physics*, 1933, **1**, 348) for the zero-point energy difference between Ni–H and Ni–D and obtained by Melville (J., 1934, 804) for the hydrogen–nitrous oxide and the hydrogen–oxygen reaction at a nickel surface. We may thus infer that the low-temperature reaction is controlled by the rate of activation of chemiadsorbed hydrogen in the form of NiH. Recent experiments by Melville and one of the authors (E. K. R., in the press) on diffusion of the isotopes through metals suggest that the actual mechanism involved is the activated migration of NiH, or more probably H, from one nickel atom to a chemiadsorbed ethylene molecule, the energy of activation for migration sufficing also for reaction. In the high-temperature region there is no difference in reaction velocity between the two hydrogen isotopes; the rate must therefore be controlled either by a reaction involving identical energies of activation for the ethylene, the negative temperature coefficient being due to desorption of the ethylene, or, more probably, by some reaction involving the hydrogen which does not involve a zero-point energy difference.

Both Langmuir (cf. *Trans. Faraday Soc.*, 1921, **17**, 607) and Roberts (*Nature*, 1935, **135**, 1037) have advanced arguments to support the view that, above a chemiadsorbed monolayer of gas on a metal surface under suitable conditions, there exists a second layer held by van der Waals forces, and Roberts has shown furthermore that the chemiadsorbed monolayer is never complete. The experiments of Melville and one of the authors, referred to above, have shown that the penetrations of both hydrogen and deuterium from the van der Waals layer into the metal proceed with identical energies of activation.

If the lower-temperature reaction involves the diffusion of hydrogen already persorbed by the metal, it is possible that at high temperatures the rate of supply of hydrogen from the van der Waals layer by penetration may limit the rate of reaction, and for this reaction both hydrogen and deuterium penetrate at equal speeds for equal densities of population in the van der Waals layer. Further experiments are required to decide between these alternatives.

SUMMARY.

It is shown that the reaction between normal and heavy hydrogen with ethylene on a nickel surface catalyst is of zero order between 0° and 17°. At low temperatures (— 23°) the velocity is extremely slow, probably on account of a very high adsorption of ethylene. The velocity coefficient of hydrogenation of ethylene with hydrogen at 0° is 1·5 times greater than that with deuterium (96% D). At high temperatures the speeds are identical. The difference in energy of activation is about 790 cals. at 0—17°, and about 500 cals. at 120—139°. Both velocity coefficients increase with rising temperature, but for hydrogen the maximum is at about 140°, and for deuterium at about 160°.

A tentative proposal for the mechanism of the reaction is given.

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