146. *The Deuteration and Exchange of Ethylene on Evaporated Metal Catalysts at Low Temperatures.*

By CHARLES KEMBALL.

Measurements have been made by a mass-spectrometric technique of the amounts of the various deutero-compounds formed during the reaction between ethylene and deuterium on evaporated films of tungsten, nickel, rhodium, and iron at −100°. The distribution of products obtained over tungsten films differed substantially from those from the other metals but was in accord with the behaviour of tungsten in the catalytic exchange of ethane and deuterium. The relative efficiencies of the metals for the deuteration of ethylene at −100° gave supporting evidence for the correlation between activity for hydrogenation at 0° and the percentage *d*-bond character of the intermetallic bonds.

The results provided new evidence for the close connection between exchange and deuteration of ethylene, and a general theory has been formulated for the calculation of the distribution of initial products in terms of four fundamental parameters associated with the adsorbed species in this reaction. Good agreement was obtained between calculated and observed distributions. Although the general theory was not based on any particular mechanism for the reaction, a method has been suggested by which it may be used to assess the part played by different mechanisms.

A RECENT investigation [1] has shown that there is a great variation in the catalytic activity of different transition metals for the exchange reaction between ethane and deuterium. Furthermore, there were differences in the initial products obtained; tungsten, molybdenum, and tantalum produced [$^2H_1$]ethane as the major initial product because a simple exchange mechanism (replacement of one hydrogen atom at a time) was operating. On rhodium and palladium a multiple exchange mechanism predominated and gave [$^2H_6$]ethane as the most abundant initial product. The present work was undertaken to see if there were corresponding differences in the amounts of olefin-exchange and in the pattern of the deuteroethanes when certain of these metals were used as catalysts for the ethylene–deuterium reaction.

The only investigations in which complete analyses of all the deutero-ethylenes and -ethanes formed in this reaction have been reported were those of Turkevich *et al.*[2] who worked with a nickel-filament catalyst at 90°, and that of Wilson *et al.*[3] who used a commercial nickel catalyst supported on kieselguhr between —50° and 50°. The importance of these complete analyses for a better understanding of the mechanisms operating in the hydrogenation and exchange of olefins has been stressed by Wilson *et al.*[3]

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[1] Anderson and Kemball, *Proc. Roy. Soc.*, 1954, *A*, **223**, 361.

[2] Turkevich, Bonner, Schissler, and Irsa, *Discuss. Faraday Soc.*, 1950, **8**, 352; Turkevich, Schissler, and Irsa, *J. Phys. Colloid Chem.*, 1951, **55**, 1078.

[3] Wilson, Otvos, Stevenson, and Wagner, *Ind. Eng. Chem.*, 1953, **45**, 1480.

and also by Bond.[4] Keii [5] has developed theoretical equations for the initial-product distributions based on the reaction mechanism favoured by Horiuti [6] and has shown that they give results in general agreement with the observations of Turkevich *et al.*[2]

A low temperature (*ca.* —100°) was chosen for the present experiments, partly in order that the rates of reaction should be low enough to allow determination of the initial distribution of products, and partly for the purpose of comparing the efficiencies of the different metals for deuteration at a temperature substantially different from that used by Beeck.[7]

EXPERIMENTAL

The preparation of the metallic films, the catalytic apparatus, and the manner in which the reacting gases were allowed to bleed into the mass spectrometer have been described.[8] Ethylene was obtained from a cylinder and purified by distillation from cold traps. Mass-spectrometric analysis showed that it contained less than 0·5% of ethane. In most of the experiments, 2·7 mm. of ethylene and 8·1 mm. of deuterium, after passage through a trap at −78° to condense mercury vapour, were admitted to the reaction vessel at approximately −120°. The volume of the reaction vessel was 180 ml. and the charge of hydrocarbon was estimated to be $2{\cdot}4 \times 10^{19}$ molecules.

Temperature control proved to be difficult. A large Dewar vessel containing the eutectic mixture of ethyl bromide, 45% (by vol.), trichloroethylene, 21%, chloroform, 20%, and dichloroethylene, 14%, was used. This mixture freezes at −139° but it was possible to keep the temperature steady within 2—3° at approximately −100° for periods of 30—45 min. by adding small quantities of liquid air to the liquid in the Dewar vessel. Temperatures were measured by a calibrated thermocouple. After a few minutes had been allowed for the gas mixture to flow into the mass spectrometer with the reaction vessel at −120°, the temperature was adjusted to −100° and readings were taken.

During each experiment, sets of readings were taken alternately of (*a*) the peaks corresponding to masses 28—32 with 11·0 v for the ionising electrons in the mass spectrometer, and of (*b*) the peaks corresponding to masses 28—36 with 13·4 v for the electrons. By interpolation, values for both sets were obtained at the same time and were corrected for the heavy carbon and deuterium occurring naturally. The fragmentation of ethylene was negligible at both voltages, but with " ethane " * ions corresponding to the loss of one or two " hydrogen " atoms occurred at both voltages. Correction to peaks of lower mass than the parent ion for fragmentation of the ethanes for mass spectra with 13·4 v on the electrons were based on the data in Table 1. In compiling this Table the fragmentations of non-deuterated ethane and $[^2H_6]$ethane were determined experimentally. The small corrections for ions formed by the loss of one " hydrogen " atom from the other ethanes were estimated by interpolation. The fragmentation for the loss of two " hydrogen " atoms for the other ethanes was assumed to occur to the same total extent as with $[^2H_6]$ethane, and the correction factors were determined by assuming that the *a priori* chance of losing a hydrogen atom [9] was 1·17 times the chance of losing a deuterium atom. As the final reaction product on tungsten films was mainly

TABLE 1. *Corrections for fragmentation to peaks corresponding to masses* X — n, *where* X *is the parent mass for ethanes with* 13·4-v *acceleration on the ionising electrons.*

X	*n* = 1	2	3	4
36	—	0·12	—	2·00
35	0·02	0·10	0·74	1·26
34	0·04	0·26	1·11	0·71
33	0·06	0·53	1·20	0·33
32	0·08	1·18	0·66	0·18
31	0·10	1·42	0·60	—
30	0·12	1·75	—	—

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* Throughout this paper, " ethane " and " hydrogen " are used as generic terms irrespective of isotopic content.

[4] Bond, *Quart. Rev.*, 1954, **8**, 279.
[5] Keii, *J. Res. Inst. Catalysis, Hokkaido Univ.*, 1953, **3**, 36; *J. Chem. Phys.*, 1954, **22**, 144.
[6] Horiuti, *Catalyst*, 1948, **2**, 1.
[7] Beeck, *Discuss. Faraday Soc.*, 1950, **8**, 118.
[8] Kemball, *Proc. Roy. Soc.*, 1951, *A*, **207**, 539; 1952, *A*, **214**, 413.
[9] Turkevich, Friedman, Solomon, and Wrightson, *J. Amer. Chem. Soc.*, 1948, **70**, 2638.

[$^2H_2$]ethane, it was possible to check the figures used for the fragmentation of that compound. The fragmentation of the ethanes at the lower electron voltage was also determined; the values were approximately half as much as those at the higher voltage.

The complete analysis of the percentages of all five ethylenes and all seven ethanes was possible because the sensitivity of the peak heights for ethanes increased 30-fold between the two voltages whereas the increase for the ethylenes was only 8-fold. In working up the results, corrections for fragmentation were applied to the values for the peaks corresponding to mass 36 down to mass 32. Corrected values of the peak corresponding to mass 32 were thus obtained at both electron voltages, and the solving of a simple pair of simultaneous equations gave the proportions of these due to [$^2H_2$]ethane and [$^2H_4$]ethylene. Corrections to the values of peaks corresponding to mass 31 were then made, and the process continued down to mass 28. The relative sensitivities for ethylene and ethane at the higher voltage were known and therefore it was possible to express the amounts of the five ethylenes and the seven ethanes as percentages of the total C_2 hydrocarbon present.

This procedure is not claimed to be of great accuracy—the greatest uncertainties were in the evaluation of the [$^2H_0$]- and [$^2H_1$]-ethanes and the [$^2H_3$]- and [$^2H_4$]-ethylenes owing to small changes in relative sensitivity if the voltage of the electrons altered. Nevertheless, the method enabled a complete analysis for the twelve C_2 hydrocarbons to be made from readings obtained in a few minutes on a simple mass spectrometer. The analyses of the ethanes obtained at the end of each run were more accurate because two or three complete sets of readings were taken and there were no contributions from ethylenes.

RESULTS

The amounts of the various ethylenes and ethanes formed during experiments on nickel, iron, rhodium, and tungsten are shown in Figs. 1—4. The plots of total percentage of ethanes against time (Fig. 5) showed that the rates of deuteration were constant throughout each run, and these plots were used to decide the position of the final analyses corresponding to 100% ethanes on Figs. 1—4. Because of the greater accuracy of the final analyses, more weight was given to these points in drawing the curves in Figs. 1—4.

Although the percentages of the deuteroethylenes of necessity varied with time in a complicated manner, it was possible to reduce the values to a linear relation from which the rate of exchange of ethylene could be determined. A quantity ϕ was defined by

$$\phi = w + 2x + 3y + 4z \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where w, x, y, z represented the percentages of ethylene present at any stage as [$^2H_1$]- to [$^2H_4$]-ethylene. Plotting of results according to the integrated form of the equation,

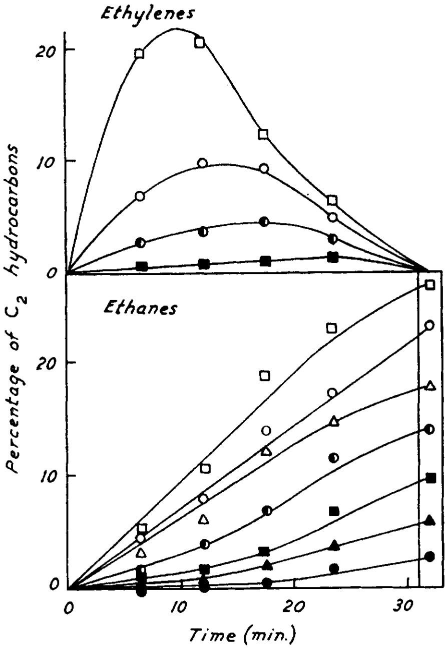
$$d\phi/dt = k\,(\phi_\infty - \phi)/\phi_\infty \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where t is time and k the initial rate of entry of deuterium atoms into 100 ethylene molecules, gave the straight lines shown in Fig. 6. As no appreciable quantities of hydrogen were returned to the gas phase (see below) to dilute the deuterium, it was justifiable to assume a value of 400 for ϕ_∞, the ultimate value of ϕ, corresponding to completely deuterated ethylene, that would have been reached had the ethylenes not been removed by deuteration. With tungsten, where the olefin-exchange was much less, the rate was found by a direct plot against time of the percentage of ethylene present as [$^2H_1$]ethylene.

The final percentages of the various ethanes obtained under different conditions, and the mean deuterium content of the ethanes, are shown in Table 2 together with corresponding results from earlier work. The proportions of HD formed during the reactions on nickel, iron, and rhodium were determined by examination of the peaks corresponding to masses 3 and 4, a sufficiently low electron voltage being used to avoid contributions due to fragmentation of the ethanes. With nickel and iron, some 1·5% of HD was formed, but with rhodium, 5% was formed. The presence of these small amounts of hydrogen in the deuterium should have been balanced by a slight excess of deuterium in the ethanes over and above the mean number of two deuterium atoms per ethane molecule. The expected values of M, based on the amount of HD present, were 2·03 for iron and nickel and 2·10 for rhodium.

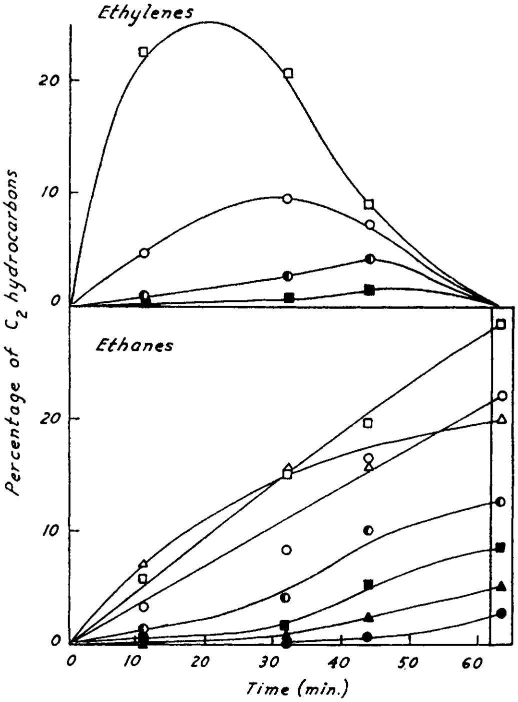
The rates of deuteration and olefin-exchange are given in Table 3 together with values of S, the coefficient of spread of the ethanes ultimately formed; S was a measure of the extent to

FIG. 1. *Reaction on 13·6 mg. of nickel at −100°.*



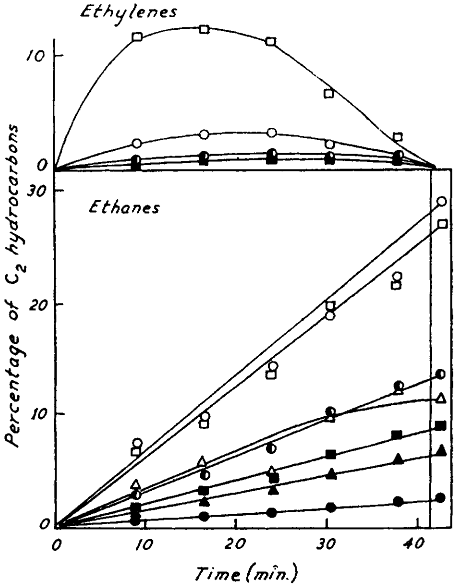
Upper graph, ethylenes; lower graph, ethanes. Final percentages of ethanes in frame. Symbols △, □, ○ ◐, ■, ▲ and ● represent compounds containing from 0 to 6 deuterium atoms.

FIG. 2. *Reaction on 10·2 mg. of iron at −100°.*



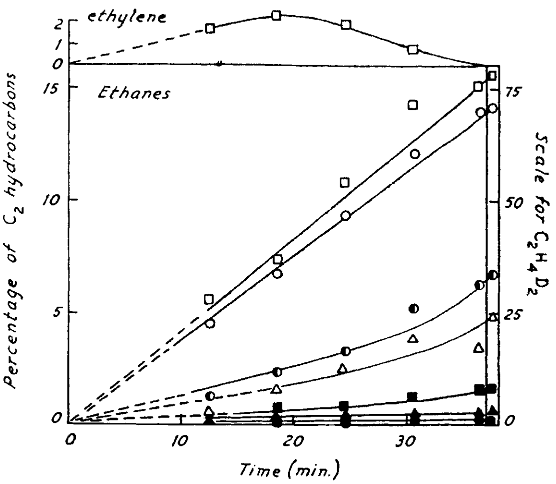
Symbols, etc., as in Fig. 1.

FIG. 3. *Reaction on 1·3 mg. of rhodium at −104°.*



Symbols, etc., as in Fig. 1.

FIG. 4. *Reaction on 7·8 mg. of tungsten at −99°.*



Symbols, etc., as in Fig. 1.

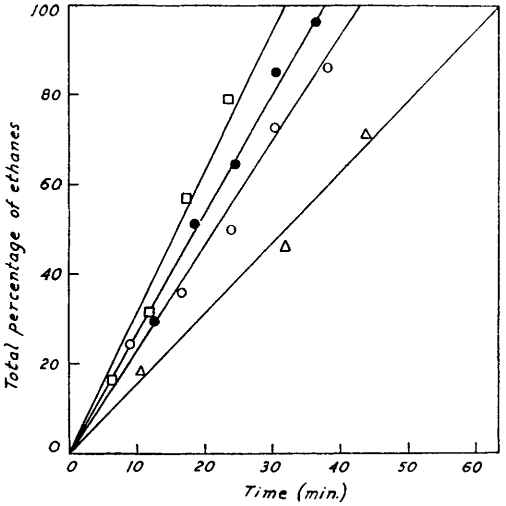
which the composition of the ethanes deviated from 100% [$^2H_2$]ethane and ranged over all values of deuterium content and was defined by

$$S = \sum_n (|n - 2|d_n)/d_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (3)$$

where d_n represents the percentage of the ethane with n deuterium atoms.

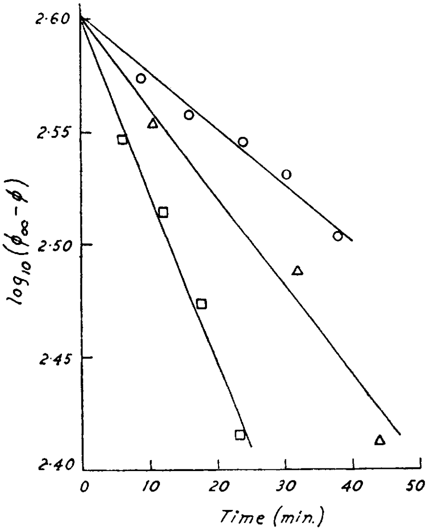
Although the temperature control was not sufficiently good to allow accurate determination of activation energies and pressure dependencies, some rough observations were noted. Ethylene-exchange and deuteration on tungsten had an activation energy of 5—6 kcal./mole between −120° and −100°, and both reactions on the other three metals had a value of 7 kcal./mole. On nickel, both reaction rates were independent of ethylene pressure and were proportional to the square root of the deuterium pressure. An experiment with ethylene alone

FIG. 5. *Total ethanes versus time for experiments in Figs.* 1—4.



□, Nickel; ●, tungsten; ○, rhodium; △, iron.

FIG. 6 *Plots of exchange of ethylene according to the integrated form of equation* (2).



Same symbols as in Fig. 5.

TABLE 2. *Percentages of various ethanes in final products and the mean deuterium number* (*M*) *of the ethanes.*

Ratio $D_2 : C_2H_4$	Catalyst	Temp.	$^2H_0$	$^2H_1$	$^2H_2$	$^2H_3$	$^2H_4$	$^2H_5$	$^2H_6$	M
3 : 1	Rh	−104°	11·5	27·2	29·1	13·7	9·1	6·8	2·6	2·10
3 : 1	Fe	−100	20·1	28·4	22·1	12·7	8·6	5·2	2·9	1·89
3 : 1	W	− 99	4·8	15·5	70·5	6·7	1·6	0·5	0·14	1·89
3 : 1	Ni	−100	17·9	26·8	23·2	14·0	9·6	5·9	2·6	1·99
9 : 1	Ni	− 92	12·4	29·9	25·4	14·3	9·7	5·9	2·4	2·06
9 : 3	Ni	− 81	17·1	30·5	20·7	13·8	9·4	6·2	2·3	1·96
10 : 1	Ni *	− 50	17·8	25·6	27·4	16·1	7·8	3·6	1·5	1·87
2 : 1	Ni †	90	8·0	29·5	25·1	16·7	11·8	6·9	2·0	2·24
Random distribution			8·8	26·3	32·9	22·0	8·2	1·7	0·14	2·00

* Supported nickel catalyst.[3] † Nickel wire.[2]

TABLE 3. *Rates of deuteration and olefin-exchange and values of the coefficient of spread* (*S*) *of ethanes formed.*

Catalyst	Temp.	Deuteration (R_1) (%/min./10 mg.)	Exchange (R_2) (D atoms/100 mol./min./10 mg.)	R_2/R_1	S
Fe	−100°	1·54	3·60	2·34	5·68
Ni	−100	2·30	5·25	2·28	5·34
Rh	−104	18·0	18·3	1·02	3·88
W	− 99	3·42	0·26	0·08	0·53

at −100° on nickel gave rise to a small percentage of ethane, in agreement with the findings of Jenkins and Rideal [10] on the decomposition of ethylene in the absence of hydrogen.

As particular interest was associated with the initial distributions of products, these were determined from the graphs together with the aid of the rates given in Table 3; the values found, expressed as percentages of total initial products, and two theoretical sets to be discussed in the next section, are listed in Table 4.

TABLE 4. *Experimental initial distributions of products and two theoretical sets of values (T_1 and T_2).*

		T_1	Ni	Fe	Rh	W	T_2
Ethylenes	$^2H_1$	41·4	46·7	55·5	34·4	7·0	5·3
	$^2H_2$	18·8	13·2	9·4	7·0	—	0·5
	$^2H_3$	6·4	2·7	1·3	1·7	—	—
	$^2H_4$	1·0	0·7	0·2	0·9	—	—
Ethanes	$^2H_0$	2·8	7·8	13·7	8·4	3·1	2·3
	$^2H_1$	9·9	12·5	9·2	14·4	14·7	23·1
	$^2H_2$	11·1	9·5	6·6	15·8	69·8	60·0
	$^2H_3$	5·7	4·0	2·4	7·4	4·5	7·8
	$^2H_4$	2·2	2·0	1·0	5·0	0·7	0·9
	$^2H_5$	0·6	0·8	0·5	3·6	0·2	0·1
	$^2H_6$	0·1	0·2	0·2	1·4	—	—

THEORY OF THE INITIAL DISTRIBUTIONS OF PRODUCTS.

As mentioned already, Keii [5] has given a theory leading to results in semiquantitative agreement with the experimental initial-product distributions of Turkevich and his co-workers.[2] This theory was based on the reaction scheme favoured by Horiuti. The only reactions taken into account in this scheme were those between chemisorbed " hydrogen " atoms, " ethyl " radicals, and " ethylene " molecules. Although this scheme has many merits, the fact that it is not generally accepted by other workers in the field constitutes a possible disadvantage of Keii's theory. A second disadvantage is that this theory leads to a complicated series of equations which can only give exact quantitative results after a number of simplifying assumptions have been made.

It is possible to develop a general theory based on the probabilities of the various changes which adsorbed entities may undergo on the surface without specifying, in the first instance, the mechanism by which these changes take place. The recent investigation [10] of ethylene adsorbed on nickel in the absence of hydrogen has shown that radicals formed by the dissociative adsorption of ethylene are rehydrogenated too slowly to play a substantial part in either olefin-exchange or hydrogenation. Consequently, the only entities which have to be considered are adsorbed ethylene and adsorbed ethyl radicals. The assumptions of the theory are as follows: (*a*) Every adsorbed ethylene molecule must either become an adsorbed ethyl radical or leave the surface. The chances of these two events are independent of isotopic content and are given by $p/(1 + p)$ and $1/(1 + p)$ respectively, p being the ratio of the chances. (*b*) When an ethylene molecule becomes an ethyl radical there is an equal change of the new " hydrogen " atom adding to either end of the ethylene molecule. The chances of obtaining a deuterium or hydrogen atom in this process are $q/(1 + q)$ or $1/(1 + q)$, respectively. (*c*) Every adsorbed ethyl radical must either revert to an adsorbed ethylene molecule or leave the surface as an ethane molecule. The chances of these two events are independent of isotopic content and are given by $r/(1 + r)$ and $1/(1 + r)$, respectively. (*d*) When an ethyl radical reverts to an adsorbed ethylene molecule, it has an equal chance of losing any of the three " hydrogen " atoms in the methyl group. (*e*) When an ethyl radical takes up a " hydrogen " atom to become a gaseous ethane molecule, the chances of obtaining a deuterium or hydrogen atom are $s/(1 + s)$ and $1/(1 + s)$ respectively.

The fractions of the products appearing as the six ethylenes—$CH_2{:}CH_2$, $CH_2{:}CHD$, $CHD{:}CHD$, $CH_2{:}CD_2$, $CHD{:}CD_2$, and $CD_2{:}CD_2$—are given the symbols A_1—A_6. For simplicity, the amounts of the ethanes formed are evaluated in terms of the fraction of

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[10] Jenkins and Rideal, *J.*, 1955, 2490.

products appearing in the gas phase as one of twelve different kinds of ethyl radical, it being understood that each is provided with a " hydrogen " atom according to assumption (*e*). The twelve ethyl radicals are $CH_2{\cdot}CH_3$, $CH_2{\cdot}CH_2D$, $CHD{\cdot}CH_3$, $CHD{\cdot}CH_2D$ $CH_2{\cdot}CHD_2$, $CD_2{\cdot}CH_3$, $CH_2{\cdot}CD_3$, $CD_2{\cdot}CHD$, $CHD{\cdot}CHD_2$, $CHD{\cdot}CD_3$, $CD_2{\cdot}CHD_2$, and $CD_2{\cdot}CD_3$ and the fractions of products represented by these are given the symbols B_1—B_{12}. Once the values of B_1—B_{12} have been determined, it is simple to convert them into fractions of product appearing as various deuteroethanes according to assumption (*e*).

By using the one fundamental generating equation [1]

$$Q_m\Big(1 + \sum_n \mu_{mn}\Big) = a_m(0) + \sum_l \mu_{lm} Q_l \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

it is possible to write down 18 simultaneous equations for the fractions A_1—A_6 and B_1—B_{12}. In equation (4) Q_m represents any of the symbols A or B, μ_{mn} is the ratio of the chance of an entity of the type m becoming an entity of the type n to the chance of m's leaving the surface, Q_l and μ_{lm} have similar meanings, and $a_m(0)$ represents the fraction of the entity present initially. As the construction of the simultaneous equations is simple they are not quoted in full but two examples are given. The equation for A_2 ($CH_2{:}CHD$) is

$$A_2(1 + p) = \tfrac{2}{3}rB_2 + rB_3 + \tfrac{1}{3}rB_4 + \tfrac{2}{3}rB_5 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and the equation for B_2 ($CHD{\cdot}CH_2D$) is

$$B_4(1 + r) = pqA_2/2(1 + q) + pA_3/(1 + q) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The 18 simultaneous equations can be solved to give the values of the fractions A and B to the third place of decimals (in times varying between 1 and 3 hr.) by the relaxation method described by Hartree.[11] The results obtained include a value for A_0, the fraction of non-deuterated ethylene in the initial product. Since this cannot be distinguished from the non-deuterated ethylene already present, it is necessary to scale up the remaining 17 fractions and express them as percentages. In working out the sets of values shown in Table 4, it is assumed that the reaction started from adsorbed $[^2H_0]$ethylene, *i.e.*, $a_m(0) = 1$ for A_1 and $a_m(0) = 0$ for all other entities.

The set of values, T_1, which gives reasonable agreement with the observations on nickel, was obtained with the following values of the parameters :

$$p = 3;\ q = 2;\ r = 12;\ s = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and the set, T_2, in reasonable agreement with the results on tungsten, with

$$p = 3;\ q = 5;\ r = 0{\cdot}4;\ s = 5 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

It is perhaps worth noting that the theory would predict the formation of $[^2H_2]$ethane alone with

$$p = q = s = \infty \text{ and } r = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

DISCUSSION

The results show that the exchange and the deuteration of ethylene are closely related reactions and that the rates of both reactions are quite rapid on films of the four metals studied at −100°. There is, therefore, a marked difference between the exchange of ethylene and the exchange of ethane for which the metals showed widely different activities. This difference in behaviour is good confirmatory evidence that the slow step in the exchange of ethane is the dissociative adsorption of the molecule. The greatest contrast is found on iron films, which are inactive for the exchange of ethane up to 370°. This is probably because further breakdown of the ethane molecule occurs in the same temperature range as dissociative adsorption of ethane on iron films.

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[11] Hartree, " Numerical Analysis," Oxford Univ. Press, 1952, p. 167.

It should be noted that no exchange of ethane is possible on any of the metals at the temperatures used in the present work and so the results in Tables 2 and 4 are due solely to the process of deuteration and exchange of ethylene. In this connection, the correlation between the ratio of exchange to deuteration and the coefficient of spread of the resulting ethanes (Table 3) confirms that the production of ethanes having more or less than two deuterium atoms is closely related to the extent of olefin-exchange taking place. This correlation may be limited to metallic films as catalysts because Wilson *et al.*[3] observed no deuteroethylenes over their supported nickel catalyst although there was a wide spread in the distribution of deuterium in the ethanes obtained. Although the activities of the metals differ widely for ethylene-exchange and ethane-exchange, there are similarities between the distribution of products obtained. The large amount of [$^2H_2$]ethane and the small amounts of deuteroethylenes formed on tungsten are in accord with the predominant part played by a simple exchange mechanism in the exchange of ethane; *i.e.*, an ethyl radical on tungsten, whether formed by dissociative adsorption of ethane or by the half-hydrogenation of ethylene has little chance of dissociating to an adsorbed ethylene molecule. The small value of r of 0·4 is a measure of this tendency and is in agreement with the value of 0·2 for a similar parameter in the work on ethane.[1] The distributions of products on the other three metals are rather similar and differ substantially from a random distribution of two deuterium atoms per ethane molecule.

The agreement between the observed values of the mean deuterium number of the ethanes in Table 2 and the values to be expected after taking into account the small amount of HD produced lends support to the reliability of the analyses. The only value of M substantially greater than 2 in that Table was that for the ethanes formed on nickel wire [2] at the high temperature of 90° where the production of HD was sufficiently rapid to allow a substantial increase in the amount of deuterium in the ethanes.

The most reliable evidence for pressure-dependence in the present work is the linear rate of production of total ethanes implying a zero order with respect to ethylene for the deuteration reaction. However, the similarity of the final distributions of products obtained with different gas mixtures over nickel is some confirmation that the kinetics of exchange and deuteration are identical.

Allowance being made for the different surface areas of the films,[8] the rates of deuteration in Table 3 can be converted into relative rates with respect to equal areas of catalyst, that for rhodium being taken as unity. These are shown in Table 5 together with Beeck's results for hydrogenation at 0°. The spread of values is much less at $-100°$ and the value for tungsten has moved up to a position intermediate between those for nickel and iron. This change of position for tungsten was not only to be expected since Beeck gave the activation energy as 2·4 kcal./mole for tungsten compared with 10·7 kcal./mole for the other metals, but also improves the correlation between catalytic activity and the product of valency times percentage of *d*-character of the intermetallic bonds first noted by Schuit [12] for this reaction.

TABLE 5. *Comparative rates of hydrogenation at* 0° *and deuteration at* $-100°$.

Catalyst	Rh	Ni	Fe	W
Hydrogenation at 0°	1	$1{\cdot}7 \times 10^{-3}$	9×10^{-4}	10^{-4}
Deuteration at $-100°$	1	$1{\cdot}1 \times 10^{-1}$	4×10^{-2}	5×10^{-2}

The mechanism of the exchange and hydrogenation or deuteration of ethylene is still a subject of some controversy and it is possible that a number of the different mechanisms that have been put forward all play a part. It was considered of importance to put forward the general theory (p. 740) not based on any particular mechanism but which, when more information is available, may indicate the extent to which different mechanisms contribute to the overall reaction. Jenkins and Rideal [10] have established that, in the absence of hydrogen, ethylene gives rise to some 80% coverage of a nickel surface by acetylenic complexes, and that half the remaining surface can be covered by chemisorbed hydrogen

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[12] Schuit, *Discuss, Faraday Soc.*, 1950, **8**, 205.

atoms in pairs. They have suggested [13] a mechanism for hydrogenation and exchange on the assumption that the whole reaction takes place on the isolated pairs of sites left after the formation of acetylenic complexes. This mechanism alone is not sufficient to account for the initial product of [$^2H_3$]- and [$^2H_4$]-ethylene observed in the present work. The presence of added hydrogen must cause a reduction in the number of acetylenic complexes and must favour the existence of the more highly hydrogenated entities such as ethylene molecules and ethyl radicals. The fact that Jenkins and Rideal [10] found no evidence for chemisorbed ethylene in the absence of added hydrogen does not preclude its existence during hydrogenation. Confirmation of, at least, the transitory existence of chemisorbed ethylene follows from the fact that some of the acetylenic complexes can be converted into ethane by adding hydrogen. However, the existence of chemisorbed hydrogen, established by Jenkins and Rideal, together with the fact that hydrogen–deuterium exchange and the ortho–para-hydrogen conversion are almost completely inhibited [14] in the presence of ethylene, comprise good evidence that neither of these reactions can take place through a complex of three " hydrogen " atoms on a single site as proposed by Couper and Eley.[15]

The mechanism put forward by Horiuti [6] makes no allowance for the Rideal type of reaction involving a gaseous molecule reacting with a chemisorbed entity which Twigg [14] claimed was necessary to explain the observed kinetics. Wilson *et al.*[3] have suggested that exchange of the olefin was achieved by the direct transfer of " hydrogen " atoms between adsorbed olefin and adsorbed alkyl radicals. They argued that, if there were appreciable quantities of hydrogen atoms on the surface, the return of hydrogen to the gas phase would be possible by the mechanism proposed by Couper and Eley, and consequently that reactions involving chemisorbed hydrogen were unimportant. This conclusion may not be valid in light of the new evidence. Wilson and his co-workers also suggested that the chance of obtaining a deuterium atom was the same when an adsorbed alkyl radical was converted into a gaseous alkane as when an adsorbed alkene was converted into an adsorbed alkyl radical; this hypothesis was introduced to account for the agreement between the observed quantities of [$^2H_0$]- and [$^2H_1$]-butane and the calculated values for a random distribution of 2·13 deuterium atoms per molecule. However, a simple calculation shows that different probabilities of obtaining a deuterium atom in the two steps can still lead to the same values for [$^2H_0$]- and [$^2H_1$]-butane provided the two probabilities continued to give a resultant chance of 2·13 deuterium atoms per molecule. For this reason, two different probabilities for these steps are included in the general theory given in this paper.

The agreement between the observed initial product distributions on nickel and tungsten and the values calculated from the general theory is very satisfactory. It is not possible at this stage to specify the part played by different mechanisms but the parameters p, q, r, and s are certainly fundamental quantities for the overall reaction, and when more information is available about the effect of gas pressures and temperature on these parameters the contributions of different mechanisms may become apparent. An interesting feature of the general theory is that it predicts not only the proportions of the different deuteroethanes but also the position of the deuterium atoms in these compounds, *i.e.*, the extent to which [$^2H_2$]ethane is composed of $CH_3{\cdot}CHD_2$ and $CH_2D{\cdot}CH_2D$. Consequently, when mass-spectrometric technique is sufficiently improved to permit the determination of all these isomers, some most illuminating results may come to light.

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[13] Jenkins and Rideal, *J.*, 1955, 2496.
[14] Twigg, *Discuss. Faraday Soc.*, 1950, **8**, 152.
[15] Couper and Eley, *ibid.*, p. 172.