870. *The Catalytic Hydrogenation of Unsaturated Hydrocarbons.   Part II.*[1] *Reaction between Dideuteroacetylene and Hydrogen over a Nickel–Pumice Catalyst.*

By G. C. Bond.

The products of the reaction between dideuteroacetylene and hydrogen over a nickel–pumice catalyst between 40° and 120° have been analysed by mass- and infrared spectrometry. All possible deuterated ethylenes were found, dideuteroethylene always predominating; their relative yields at constant temperature were not markedly dependent on the hydrogen : acetylene ratio, but the proportion of dideuteroethylene fell with increasing temperature. Only about 5% of the dideuteroethylene was in the asymmetric form, but the ratio of the *cis*- to the *trans*-form fell from about 4·0 at 40° to 2·0 at 100°.

A simple theoretical scheme involving only two disposable parameters accounts very satisfactorily for the observed ethylene distributions, including the ratio of asymmetric to symmetric dideuteroethylene. A fraction $s/(1 - s)$ measures the chances of any adsorbed acetylene molecule or vinyl radical's gaining a hydrogen atom as against a deuterium atom, and $p/(1 - p)$ determines the relative chances of a vinyl radical's becoming ethylene or reverting to acetylene. Values of s are independent of temperature but increase with increasing hydrogen : acetylene ratio, while the reverse is true for values of p. The relevance of the results to the mechanisms suggested in Part I[1] is discussed.

ALTHOUGH deuterium has been widely employed to obtain a better understanding of the mechanisms of olefin hydrogenation and hydrocarbon exchange,[2] it has been little used to study processes involved in the hydrogenation of the acetylenic triple bond. Farkas and Farkas,[3] working with a platinum catalyst at 20°, found that the exchange reaction $C_2H_2 + D_2 \longrightarrow C_2HD + HD$ proceeded to only a negligible extent. Arnett and Crawford[4] attempted the synthesis of *cis*-dideuteroethylene from acetylene and deuterium by means of a palladium catalyst, but obtained all possible deuteroethylenes. The same object caused Douglas and Rabinovitch[5] to study the system in greater detail using a nickel–kieselguhr catalyst. They found that, while acetylene and deuterium interacted at room temperature to give approximately equal yields (20—25% each) of the *cis*- and the *trans*-isomer of dideuteroethylene, lowering the temperature to −80° greatly

[1] Part I, *J.*, 1958, 2705.
[2] See for example Bond, *Quart. Rev.*, 1954, **8**, 279.
[3] Farkas and Farkas, *J. Amer. Chem. Soc.*, 1939, **61**, 3396.
[4] Arnett and Crawford, *J. Chem. Phys.*, 1950, **18**, 118.
[5] Douglas and Rabinovitch, *J. Amer. Chem. Soc.*, 1952, **74**, 2486.

increased the yield of *cis*-isomer. The use of equilibrated and non-equilibrated hydrogen–deuterium mixtures to effect the reduction resulted in very similar distributions of products.

I have now studied this system further by more careful analysis and over a wider range of conditions. I expected that the results would assist the interpretation of the kinetics found in Part I. Since the preparation of fairly pure dideuteroacetylene is straightforward, I decided to introduce the tracer element into the acetylene rather than the hydrogen.

EXPERIMENTAL

The apparatus and general procedures were as described in Part I,[1] and the same samples of catalyst were used.

Reactants.—Hydrogen and acetylene were treated as before.[1] Dideuteroacetylene was prepared from heavy water (99.7% D_2O) with well-outgassed calcium carbide, by the standard method.[6] The product, analysed mass-spectrometrically, contained 96.0% of C_2D_2 and 4.0% of C_2HD, corresponding to an isotopic purity of 98.0%. Ethylene (British Oxygen Company) and ethane (Chemical Research Laboratory) were outgassed and used to calibrate the mass spectrometer without treatment.

Procedure.—Before each experiment, the catalyst was pretreated with 20—25 mm. of C_2D_2 for not less than 25 min., after which the reaction vessel was pumped for 10 min. The reactants were then admitted, the C_2D_2 being added first (unless otherwise stated), followed by the hydrogen 2 min. later. After the reaction had proceeded to the desired extent, the contents of the reaction vessel were passed through a trap at −196°, where the condensable products were pumped until the unchanged hydrogen had been removed; they were then transferred to a cooled Ward still.[7] An ethylene and ethane fraction (containing a small amount of acetylene) was collected at −183°, and in some experiments the main acetylene fraction was taken at −145°. Mass-spectrometry showed that, unless this distillation technique was used, fragments formed from C_4, C_6, and higher hydrocarbons present in the sample gave rise to ions in the C_2 region, and that these ions seriously interfered with the ethylene–ethane analysis; however at neither of the two distillation temperatures did any detectable amounts of hydrocarbons higher than C_2 distil.

The catalyst was kept under a slight pressure of hydrogen between experiments.

Mass-spectrometry.—The instrument has been fully described;[8] low-energy electrons (nominally 12.7 v, uncorrected for contact potentials) were employed. Average values for the relative positive-ion currents of masses 26—32 (excepting 28) were probably accurate to better than 1%. Mercuric acetate solution was used to remove part of the ethylene from ethylene–ethane mixtures, and the difference between the suitably normalised mass spectra of samples before and after this treatment was therefore the ethylene mass spectrum.

Infrared Analysis.—Selected samples, after distillation, were introduced into a 10 cm. cell having rock-salt plates, and their infrared spectra obtained using a Grubb-Parsons double-beam spectrometer at 25°; cell pressures were 25 mm. or less.

RESULTS

Mass-spectra of Hydrocarbons at Low Voltage.—The use of low-voltage electrons greatly simplifies the mass-spectra of hydrocarbons, as is seen from the annexed figures where a typical mass-spectrum for ethylene at 12.7 v is compared with that recorded in the A.P.I. tables[9] (50 v; in parentheses). At 12.7 v, ions other than the parent are absent from acetylene,[10] and the parent ion $C_2H_4^+$ was formed 3.24 times as readily as the parent ion $C_2H_6^+$ in ethylene–ethane mixtures.

Mass	28	27	26	25	24
Relative ion currents at 12.7 v	100 (100)	4.00 (62.3)	9.71 (61.2)	— (11.5)	— (3.0)

Calculation of Ethylene Compositions.—The principles of calculation are well known. In setting up the simultaneous equations I assumed that the relative probabilities of loss of atoms of

[6] Bond, Sheridan, and Whiffen, *Trans. Faraday Soc.*, 1952, **48**, 715.
[7] Ward, *Ind. Eng. Chem.*, 1938, **10**, 169.
[8] McElcheran, Ph.D. thesis, Leeds, 1954: Dainton and McElcheran, *Trans. Faraday Soc.*, 1955, **51**, 657.
[9] American Petroleum Institute, Project 44, "Tables of Mass Spectral Data."
[10] Field, Franklin, and Lampe, *J. Amer. Chem. Soc.*, 1957, **79**, 2665.

hydrogen and deuterium from all species were equal, and that likewise the probabilities of losing 2H, HD, and 2D were equal. The validity of these assumptions was shown by comparing the observed with the expected (in parentheses) mass-spectrum at 12·7 v of *trans*-dideutero-ethylene, a pure sample of which was kindly provided by Professor B. S. Rabinovitch of the University of Washington. The agreement is satisfactory.

Mass	30	29	28	27	26
Obs. (calc.)	100 (100)	3·6 (1·8)	4·2 (3·7)	4·4 (5·8)	0·8 (1·4)

Effect of Variation of Hydrogen Pressure.—A series of experiments was carried out at

TABLE 2. *Effect on the distribution of products of varying the initial hydrogen pressure, after 77—78% reaction at 97·5° ± 0·1°.*

Hydrogen pressure (mm.)	Initial pressure of C_2D_2, 100·6 ± 0·6 mm.					
	C_2D_4	C_2HD_3	$C_2H_2D_2$	C_2H_3D	C_2H_4	Deuterium no.
147·7	2·6	21·6	57·4	15·4	3·0	2·09
431·5	1·9	17·3	59·2	19·4	2·3	2·01

Effect of Variation of Acetylene Pressure.—Experiments were carried out at the same temperature with a fixed initial pressure of hydrogen (38 ± 1 mm.) and a variable excess of pressure of C_2D_2; two analyses were again made for each set of conditions, and the results are shown in Table 3. In every case the deuterium number is significantly greater than 2, and increases with

TABLE 3. *Effect on the distribution of products of varying the initial C_2D_2 pressure at 97·3° ± 0·2°.*

Reaction (%)	C_2D_2 pressure (mm.)	C_2D_4	C_2HD_3	$C_2H_2D_2$	C_2H_3D	C_2H_4	Deuterium no.
39 ± ½	72·8	1·9	21·0	61·8	14·2	1·2	2·12
,,	146·5	2·3	22·3	59·0	14·9	1·4	2·13
68 ± 3	74·8	2·1	22·3	60·0	14·3	1·3	2·14
,,	141·3	3·6	24·2	56·0	14·1	2·0	2·17

increasing amount of reaction: thus although the C_2HD formed is diluted in the excess of C_2D_2, the relative rate of the exchange reaction also increases as the $C_2D_2 : H_2$ ratio rises, the latter being the dominant effect. However the change in composition of the product through the reaction is only really significant when the initial $C_2D_2 : H_2$ ratio is about 3·5: here the yields of C_2D_4 and C_2HD_3 rise, while that of $C_2H_2D_2$ falls, as the reaction proceeds.

Effect of Temperature Variation on the Distribution of Products.—The yield of $C_2H_2D_2$ increases with decreasing temperature (Table 4), and this is accompanied by a corresponding decrease in the yield of C_2HD_3, the other products being almost unaffected: as a result, the deuterium number also falls with decreasing temperature. The inference is therefore that below about 95° the hydrogen exchange predominates, whereas above this temperature acetylene exchange predominates.

TABLE 4. *Effect of temperature on distribution of products with 36·4 ± 0·5 mm. of C_2D_2 and 92·2 ± 1·7 mm. of hydrogen (ratio 2·53 ± 0·08), after 39 ± 1% of reaction.*

Temp.	C_2D_4	C_2HD_3	$C_2H_2D_2$	C_2H_3D	C_2H_4	Deuterium no.
58·0°	1·2	9·6	67·3	19·8	2·1	1·92
77·0	1·4	13·0	63·6	19·4	2·6	1·95
97·3	1·3	16·8	61·1	19·1	1·7	2·01
118·0	1·6	18·2	59·6	18·6	2·0	2·03

A further series of experiments was carried out with a larger pressure of C_2D_2, chiefly to obtain sufficient products for infrared analysis, but mass-spectrometric analyses were also performed, and the results are recorded in Table 5. The trend of the results is very similar to that shown in Table 4 because the larger C_2D_2 pressure causes an increase in the yield of C_2HD_3 and a decrease in $C_2H_2D_2$ (Table 2), while the larger hydrogen pressure reverses these effects (Table 1) which therefore almost cancel each other.

TABLE 5. *Effect of temperature on the distribution of products with 100·6 ± 0·6 mm. of C_2D_2 and 500·5 ± 3·5 mm. of hydrogen, after 77—80% of reaction.*

Temp.	C_2D_4	C_2HD_3	$C_2H_2D_2$	C_2H_3D	C_2H_4	Deuterium no.
40·7°	1·3	7·8	70·2	17·8	2·9	1·91
58·0	1·8	10·1	65·6	19·5	3·0	1·92
80·7	1·6	15·9	61·7	18·8	2·0	2·00
97·7	1·9	17·3	59·1	19·4	2·3	2·01

Acetylene Exchange.—The ethylene analyses imply that with initial $H_2 : C_2D_2$ ratios of less than about 2·5 at 97°, there is an overall acetylene exchange reaction leading to the formation of gaseous C_2HD. To confirm this, the acetylene fractions from six runs at 97·3° were analysed mass-spectrometrically; C_2HD constituted between 6 and 8% of the total acetylene in all

cases.   After expressing the results in terms of partial pressures, I obtained initial rates of
formation of C_2HD, allowing for the removal of the C_2HD originally present.   After correction

TABLE 6.   *Dependence of the relative rate of formation of* C_2HD *on pressure of* C_2D_2 *at* $97\cdot3°$.

Hydrogen pressure (mm.)	C_2D_2 pressure (mm.)	$+d[C_2HD]/dt$ (mm./min.)	$-dP/dt$ (mm./min.)	$\dfrac{+d[C_2HD]/dt}{-dP/dt}$
68·5	36·0	0·065	1·60	0·04
38·0	74·0	0·060	0·50	0·12
38·0	144·0	0·200	0·55	0·36

for varying initial rates of fall of pressure, the dependence of the relative rate of formation of
C_2HD on C_2D_2 pressure was found (Table 6): the rate of formation of C_2HD in the first run of
this series may be somewhat depressed by the higher hydrogen pressure.   These results can be
quite accurately expressed in the form

$$\text{Relative rate of formation of } C_2HD \propto [C_2D_2]^{1\cdot2}$$

Acetylene exchange is therefore of small importance.
    Further confirmation of this view was obtained by allowing a mixture of $17\cdot3$ mm. of C_2H_2
and $20\cdot3$ mm. of C_2D_2 to react with $91\cdot4$ mm. of hydrogen at $97\cdot3°$, and analysing the products
after 40% of reaction.   The initial and final compositions of the acetylene fraction were
C_2H_2, $46\cdot0$ and $45\cdot1$; C_2HD, $2\cdot2$ and $4\cdot1$; C_2D_2, $51\cdot8$ and $50\cdot8\%$ respectively.   The amount of
equilibration between the acetylenes is seen to be very slight, and there is no change in the
deuterium number, both results demonstrating the relative unimportance of the acetylene
exchange reaction under these conditions.   It is known that isotopic exchange occurs between
C_2H_2 and C_2D_2 on this catalyst, which is however rapidly poisoned for this reaction by hydro-
genation.[6]   In the experiment immediately preceding the one described above, a similar mix-
ture was allowed to react in the absence of hydrogen at the same temperature, the catalyst
having been pretreated with acetylene to remove adsorbed hydrogen; after 1 hr. the C_2HD
content had risen from $2\cdot2\%$ to $4\cdot4\%$.   This catalyst sample had previously been used for
some 200 hydrogenations.   The presence of hydrogen therefore increases the rate of formation
of C_2HD about three-fold.
    The composition of the ethylenes obtained from the hydrogenation of the C_2H_2–C_2D_2 mixture
was: C_2D_4, $1\cdot1$; C_2HD_3, $5\cdot4$; $C_2H_2D_2$, $32\cdot8$; C_2H_3D, $17\cdot7$; C_2H_4, $43\cdot0\%$, the deuterium number
therefore being $1\cdot04$.
    Reaction of Dideuteroacetylene with Adsorbed Hydrogen.—Acetylene and adsorbed hydrogen
immediately formed some ethylene, but no ethane.[1]   To discover more about the mechanism of
this process, a similar experiment was carried out at $97°$ with $24\cdot5$ mm. of C_2D_2: a sample was
taken after 25 min. and analysed in the mass-spectrometer.   It consisted chiefly of C_2D_2, and
this therefore precluded the estimation of any C_2H_4 which might have been present.   How-
ever all the possible deuteroethylenes were detected, and they were estimated as C_2D_4, 16;
C_2HD_3, 30; $C_2H_2D_2$, 35; C_2H_3D, 19%.   Owing to the small quantity of ethylenes formed, this
analysis must be regarded as only approximate ($\pm5\%$), but nevertheless the formation of
ethylenes other than that expected from the direct addition of two adsorbed hydrogen atoms to
an acetylene molecule has definitely been established.
    Determination of the Relative Proportions of the cis-, trans-, *and Asymmetric Isomers of
Dideuteroethylene.*—The spectrum of the distilled products of an early run ($100\cdot1$ mm. of C_2D_2
and $501\cdot2$ mm. of hydrogen at $58\cdot0°$ to 80% conversion) was recorded from 2 to 15 μ at 25 mm.,
and the frequencies of the principal absorption maxima agreed within the error of measurement
with the literature values for the deuterated ethylenes.[4, 11]   The spectrum of pure *trans*-$C_2H_2D_2$
was also run over the same wavelength range at 12 mm. pressure, and the observed frequencies
of the absorption maxima again agreed well with literature values.[11, 12]
    The bands chosen for use in estimating the relative proportions of the isomers were the ω_7
modes of each species, which are at 726 cm.$^{-1}$ for *trans*-$C_2H_2D_2$, 751 cm.$^{-1}$ for *asym*-$C_2H_2D_2$ and
842 cm.$^{-1}$ for *cis*-$C_2H_2D_2$.   In the cases of the *cis*- and *trans*-isomers, contributions from the
ethylenes other than $C_2H_2D_2$ appeared to be negligible at these frequencies: percentage
transmissions for these bands were therefore taken from the theoretical base line.   The 751 cm.$^{-1}$

[11] Charette and de Hemptinne, *Bull. classe sci. Acad. roy. Belg.*, 1951, **37**, 436.
[12] Crawford, Lancaster, and Inskeep, *J. Chem. Phys.*, 1953, **21**, 678.

band of asym-$C_2H_2D_2$ is superimposed on the fine structure of the 726 cm.$^{-1}$ band of the *trans*-isomer, and transmissions were calculated from a line drawn across the base of the peak. Most samples were run both before and after the cell had been filled to atmospheric pressure with dry air: the addition of air always decreased the transmission.

The spectrum of the products of the early run was obtained at several different pressures both in the presence and in the absence of air: plots of the negative logarithm of the transmissions against pressure were then constructed for the three isomers. The basic assumption was then made that the extinction coefficients of the three chosen bands could be taken as equal. This is perhaps more likely to be true than if bands corresponding to differing modes had been employed. The analysis of this early run at once followed from this assumption, and thereafter the interpolation of any observed transmission into the appropriate Beer's law curve yielded the partial pressure of that isomer: a complete analysis was thus readily obtained.

The results are given in Table 7. Analyses of runs performed under similar conditions gave closely concordant results (see runs A-233 and A-235): the yields of the three isomers vary fairly smoothly with variation in temperature, but at 97° they appear to be independent of

TABLE 7. *Dependence of the relative proportions of* cis-, trans-, *and* asym-$C_2H_2D_2$ *on temperature and partial pressure.*

Reaction, 77—80%. Initial $H_2 : C_2D_2$ ratio (excepting run A-234), 4·65 ± 0·40.

Run	Temp.	Hydrogen pressure (mm.)	C_2D_2 pressure (mm.)	Composition of $C_2H_2D_2$ (%)		
				cis	*trans*	*asym*
B-49	40·7	504·0	100·0	77·5	20·6	1·9
A 237	41·7	338·3	74·2	74·2	22·8	3·0
A-202	58·0	501·2	101·1	75·0	22·3	2·7
A-236	80·7	497·2	100·3	67·7	28·2	4·1
A-235	97·7	431·5	101·2	64·6	30·7	4·7
A-233	97·1	453·1	100·3	64·2	30·7	5·1
A-234	97·4	147·7	100·0	63·5	32·5	4·0

partial pressure variation (runs A-233—A-235). At about 41° there is evidence that a lower total pressure gives a slightly lower degree of stereospecificity than a higher one (runs B-49 and A-237). However, while the reproducibility is satisfactory, the absolute values of the proportions of the isomers may be considerably in error: measurements of the transmissions may be inaccurate, for it is known that, at least for other bands of these isomers, the intensity

This work has emphasised the large differences in behaviour between ethylene and acetylene in their hydrogenation over nickel catalysts. In the reaction between ethylene and deuterium, much olefin- and hydrogen-exchange occurs, and their unequal initial occurrence leads to a varying isotopic content of the reactants and hence to changing proportions of deuteroethanes through the reaction.[2] Owing to the greater strength of adsorption of acetylene, the acetylene-exchange process is relatively less important. The reason for the smaller occurrence of hydrogen-exchange finds several possible explanations (see below). However, as the empirical isotopic composition of the ethylene never departs from the stoicheiometrically-expected value by more than about 8%, the distributions of products are generally sensibly constant throughout a reaction. They are not critically dependent upon the initial hydrogen : acetylene ratio used, and it is therefore inferred that the concentrations of adsorbed species are not very sensitive to changes in this ratio, as expected if acetylene is considerably more strongly adsorbed than hydrogen.

Distribution of Deuteroethylenes.—I now attempt a quantitative interpretation of the observed distributions of ethylene in terms of the mechanisms put forward in Part I.[1] There it was suggested that chemisorbed acetylene and hydrogen atoms rapidly interact to form vinyl radicals, which subsequently disproportionate to ethylene and adsorbed acetylene, as

$$2C_2X_3 \longrightarrow C_2X_4 + C_2X_2 \qquad \qquad \cdots \cdots \cdots \cdots \quad (1)$$

where X represents either H or D. Depending on whether the vinyl radical gaining the X atom is at the time in the normal or the free-radical form,[15] the ethylene formed in this step may be automatically desorbed or may remain adsorbed.[16] If the latter, it may either desorb or suffer further hydrogenation to ethane; it will be assumed that the ratio of the chances of these processes' occurring [9] is independent of the isotopic content of the ethylene. The occurrence of the further hydrogenation of some of the chemisorbed ethylene may therefore be ignored.

The results are interpreted by use of a suitably modified form of the method used by Kemball[17] for the ethylene–deuterium reaction on metal films. No specific mechanism is assumed, but the scheme is consistent with the mechanism outlined above. It is supposed that in the steady state there exist on the surface concentrations a_2, a_1, and a_0 of the acetylenes C_2D_2, C_2HD, and C_2H_2. Each has the same chance (q) of gaining a hydrogen atom and the same chance ($1 - q$) of gaining a deuterium atom: the origin of these atoms is irrelevant. No provision need be made for the desorption of acetylenes. There are equal chances of the addition of the atom to either end of any acetylene. In this manner the six possible vinyl radicals are formed, and each radical has the same chance (p) of gaining another hydrogen atom (chance s) or another deuterium atom (chance $1 - s$) forming ethylene, or of losing a hydrogen or deuterium atom (chance $1 - p$) and reverting to an acetylene. Thus the relative rates of formation of the six ethylenes (*sym-* and *asym-*

calculations demanded an interdependence between (i) the fraction (α) of dideuteroethylene in the asymmetric form and the total yield of dideuteroethylenes ($\sum e_2$) and (ii) the deuterium number and $\sum e_2$. The senses of these relationships were in harmony with observations.

For the distribution to be symmetrical (*i.e.*, for a deuterium number of 2·00), the relation $R = (1 - s)/(1 - p) = 0.33$ has to be obeyed. Deuterium numbers less than

Fig. 1. *Theoretical inter-relationships between $\sum e_2$, R, p, and deuterium number. The near-horizontal lines give the dependence of $\sum e_2$ on R at constant p, while the curves (labelled with the deuterium numbers) give the dependence of $\sum e_2$ on R at constant deuterium number.*
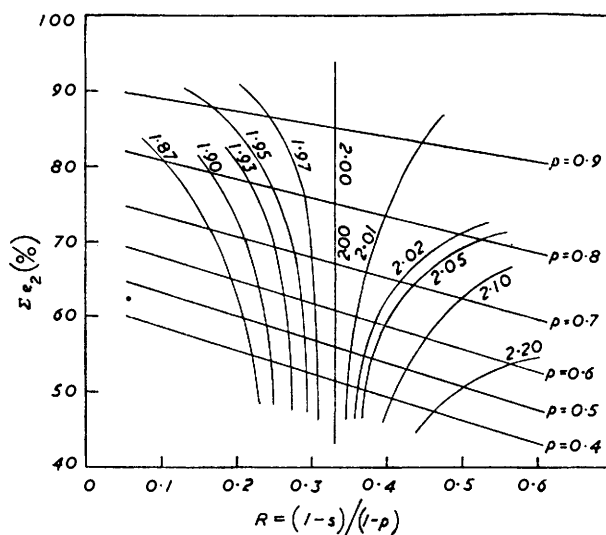
2 result when $R < 0.33$, the precise value depending both on R and on the actual values of s and p. Correlating graphs were then drawn, in which the percentage yields of the various deuteroethylenes, α, and the deuterium number were plotted against R at various values of p and against p at various values of R. (Further information concerning the scheme and graphs can be obtained from the author.) The theoretical distribution arising from any pair of values of s and p could then be rapidly obtained by interpolation.

The kind of agreement obtained between calculated and experimental values of the various quantities is shown by three quite typical examples in Table 8. Values of s and p were obtained as follows. Fig. 1 shows the master-graph relating $\sum e_2$, the deuterium number, R, and p: thus for any chosen value of $\sum e_2$ or deuterium number there are an infinite number of conjugate values of R and p, but for every conjugate pair of values of $\sum e_2$ and deuterium number there are unique values of R and p, given by the points of intersection of the lines. Values of R and p were therefore selected by interpolation to

TABLE 8. *Comparison between observed and calculated values of variables.*

Location	s	p	C_2D_4	C_2HD_3	$\sum e_2$	C_2H_3D	C_2H_4	α	$\sum e_i$	Deuterium no.
Table 4, entry 4	—	—	1·6	18·2	59·6	18·6	2·0	—	100	1·99
	0·84	0·57	1·4	18·3	59·5	20·2	1·0	5·5	100·4	2·00
Table 5, entry 1	—	—	1·3	7·8	70·2	17·8	2·9	1·9	100	1·87
	0·88	0·68	0·2	8·0	70·3	20·0	1·3	2·0	99·8	1·85
Table 3, entry 2	—	—	2·3	22·3	59·0	14·9	1·4	—	100	2·09
	0·73	0·62	2·5	21·2	59·0	16·8	1·1	5·5	100·6	2·08

correspond as closely as possible to their observed values. From the value of p, and of s corresponding to R, the remaining five observable variables were independently calculated from the correlating graphs. The five variables are truly independent, since the restriction

that $\sum e_i = 100$ was not imposed: but $\sum e_i$ was always within about 0·5% of 100. However, the value of s is only strictly relevant to the particular isotopic composition of acetylene used in this work. In Table 8 its values were chosen to correspond to the uncorrected rather than the corrected deuterium numbers: they would have been slightly lower had the acetylene been isotopically pure.

In several typical cases the scheme reproduces the experimental results very satisfactorily. Particularly heartening is the agreement between the observed and calculated values of α (rows 3 and 4 in Table 8). Calculated values of α were obtained by the same method for the results given in Tables 2, 5, and 7; they are compared with the observed values in Table 9. The calculations based on values of s and p giving optimum agreement with $\sum e_2$ and deuterium number in the relevant experiment thus reproduce not only the qualitative trend of α with temperature but also the absolute values with gratifying accuracy. This suggests (but does not prove) that the accuracy of the experimental values of α is perhaps greater than was believed.

The values of s and p on which the calculated values of α in Table 9 are based are plotted as a function of temperature in Fig. 2. Now most experiments in Tables 5 and 7 were
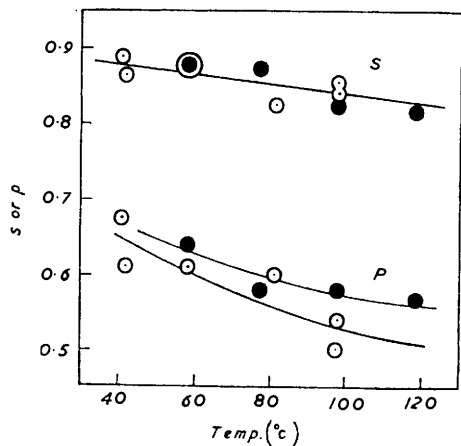

FIG. 2. *Dependence of s (upper curve) and p (lower curve) on temperature.*

⊙ Initial $H_2 : C_2D_2$ ratio, 4·65 ± 0·35 (Tables 4, 5, and 7).
● Initial $H_2 : C_2D_2$ ratio, 2·5 (Table 4).

performed (A-234 and A-237 are exceptions) with initial acetylene pressures of about 100 mm. and 430—500 mm. of hydrogen. Values of s and p have also been calculated for the results in Table 4 (where the initial hydrogen : acetylene ratio is 2·5) and these also are plotted in Fig. 2. As expected, in both series s is almost independent of increasing

TABLE 9. *Comparison between observed and calculated values of α at various temperatures.*

Run	B-49	A-237	A-202	A-236	A-235	A-233
Temp.	40·7°	41·7°	58·0°	80·7°	97·7°	97·1°
α (obs.)	1·9	3·0	2·7	4·1	4·7	5·1
α (calc.)	2·5	3·2	2·9	4·2	5·6	6·3

temperature while p declines substantially. Hence the activation energy for the conversion of a vinyl radical into ethylene must be less than that for its reversion to acetylene.

Best values of s and p, calculated from Fig. 1 for all results obtained near 97° (Tables 1—5), are plotted against initial hydrogen : acetylene ratio in Fig. 3. Values of s rise smoothly until the reactant ratio is about 2, and thereafter remain constant: values of p show a considerable scatter but may be taken as independent of reactant ratio when this exceeds unity. These trends are in the expected sense. Fig. 1 shows why the scatter of points is greater in the case of p. Of the observable quantities used in determining s and p the deuterium number is probably in error by no more than ±1% while $\sum e_2$ may be uncertain by ±3%. This uncertainty in $\sum e_2$ and no error in the deuterium number

being assumed, p will vary by $\pm 0\cdot 04$ while s only varies by $\pm 0\cdot 01$: the " brackets " in Fig. 3 accommodate these uncertainties.

The source of the hydrogen and deuterium atoms used in this treatment must be briefly considered. If it was molecular hydrogen, then s would be unity and *sym*-dideutero-ethylene the sole product: if vinyl radicals, then s should be about $0\cdot 5$. That s is about $0\cdot 84$ at $100°$ (Figs. 2 and 3) suggests that atoms come from both sources.

FIG. 3. *Dependence of s (upper curve) and p (lower curve) on initial* $H_2 : C_2D_2$ *ratio at about 97°* c.

Open points, from Table 1; hatched points, from Table 2; full points, from Table 3; ▢▪, Run A-233 (Table 7); ◗, from Table 4.

Circles refer to measurements made after about 39% of reaction, and squares after about 78% of reaction.
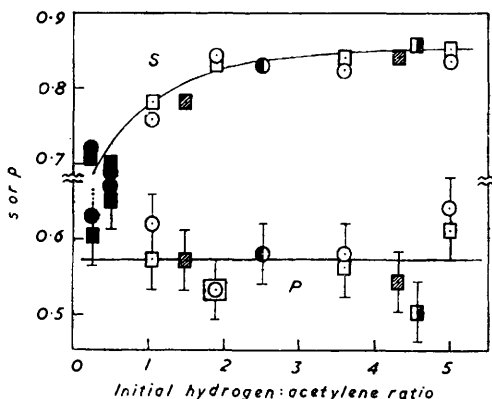
The minor importance of hydrogen-exchange may be partly explained by the low concentration of adsorbed hydrogen and deuterium atoms in the steady state, and partly by the reluctance of vinyl radicals to interact as

$$2C_2X_3 \longrightarrow 2C_2X_2 + X_2 \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2)$$
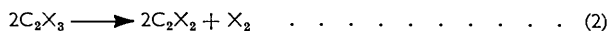
Such a process may well be more endothermic than the corresponding interaction of adsorbed ethyl radicals.

Kemball has suggested [17] that interesting results can be obtained when the precise location of deuterium atoms in hydrocarbon molecules formed in heterogeneous reactions can be determined. Unfortunately considerable rearrangement occurs under electron impact,[18] and mass-spectrometry may be useless in this connection. However in the acetylene system the positional isomers of dideuteroethylene are fairly readily distinguish-able by infrared spectroscopy, and the simple theory satisfactorily accounts for their relative abundances. This generalised theoretical approach has considerable merit, and the acetylene system is a promising field in which to test it further.

The relevance of these findings to the mechanisms proposed in Part I must now be considered. The scheme of calculation is consistent with the process whose rate constant was termed k_1: however, no sharp change in the composition of the products has been detected above $P_H°$, and it is therefore concluded that the second mechanism gives rise to deuteroethylenes having essentially the same distribution as those formed through mechanism 1. Mechanism 2 cannot then be simply the direct addition of molecular hydrogen as was suggested in Part I. The dilemma has not been completely resolved, but it is suggested that mechanisms 1 and 2 differ only in that the latter is initiated by *molecular* hydrogen and the former by dissociated hydrogen atoms, and that these two processes may be kinetically independent.
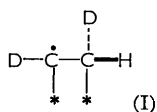
Stereospecificity.—The above procedure makes no attempt to treat the stereochemistry of the addition. Table 7 showed that the stereospecific formation of *cis*-dideuteroethylene was not achieved under any conditions, although the proportion of the *cis*-isomer rose with decreasing temperature, so I must show how both isomers may arise and why the *trans*-isomer may not be formed in more complex acetylenic molecules.[14]

[18] See, for example, McFadden and Wahrhaftig, *J. Amer. Chem. Soc.*, 1956, **78**, 1572.

In the normal form of the vinyl radical, all the atoms (including the metal atom on which it is adsorbed) are coplanar. Now if acetylene is chemisorbed as a *cis*-ethylenic–surface complex, the addition of a hydrogen atom must yield a vinyl radical in which the hydrogen atom is *cis* to the metal atom (3):

$$\text{(3)}$$
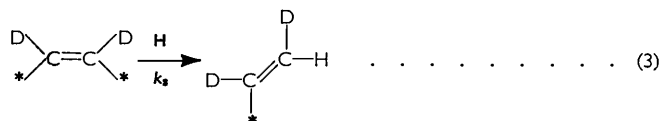
The simple addition of a further hydrogen atom yielding desorbed ethylene will likewise necessarily lead to the *cis*-isomer. Stereospecificity will be lost as soon as the double-bond is broken, so that if this last process takes the alternative path (4), the ethylenes on desorption will be an equilibrium *cis–trans* mixture if the intermediate free radical survives long enough to allow of free rotation about the C–C bond. Stereospecificity is automatically lost if the vinyl radical assumes the free-radical form (I) since the configuration of atoms about the carbon bearing the odd electron is planar: addition of the hydrogen atom from behind will give adsorbed *trans*-dideuteroethylene, and from in front *cis*. Ethylene formed through the free-radical form of the vinyl radical will therefore be an equilibrium mixture of *cis*- and *trans*-isomers:

$$\text{(4)}$$
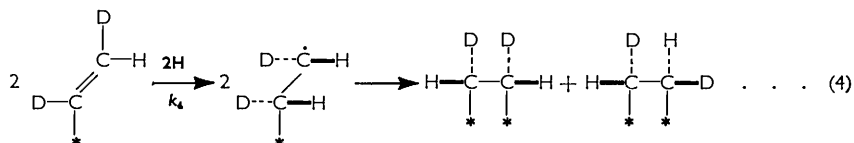
Since the free-radical form of the vinyl radical initiates the polymerisation, it is doubtful whether it gives rise to ethylene. If it does not, the degree of stereospecificity is then merely a question of the relative rates at which the carbon–metal bond and the π-bond break when a deuterium atom interacts with a vinyl radical, that is, it is simply a function of k_3/k_4. The results show that $k_3 = k_4$ at about 60° and $E_4 > E_3$.

$$\text{(5)}$$
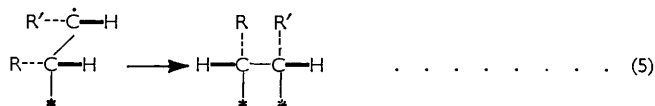
Radicals of the type CRH–ĊR'H arising from disubstituted acetylenes may be unable to undergo the necessary free rotation owing to interference between R' and the surface or other adjacent adsorbed molecules. The adsorption would then have to be stereospecific (5), and the *trans*-isomer cannot be formed. The stereospecificity of the hydrogenation of substituted acetylenes is thus logically interpreted.

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