STUDIES IN HETEROGENEOUS CATALYSIS

PART 5—EXCHANGE REACTIONS INVOLVING DIDEUTERO-ACETYLENE

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The reaction $C_2H_2 + C_2D_2 = 2C_2HD$ proceeds to equilibrium over a nickel catalyst in a few hours at 60° C. The individual acetylenes were estimated using their infra-red absorption spectra, whence K was found to be 3·2 ± 0·5 from 60-120° C. A satisfactory rate equation is

$$d[C_2HD]/dt = k(3{\cdot}2[C_2H_2][C_2D_2] - [C_2HD]^2).$$

The rate varies as the 0·65 power of the total pressure, and the activation energy is 10·7 kcal.

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C_2D_2 exchanges with one hydrogen atom of methylacetylene, but not with either ethylene or allene. For this reaction, the rate varies as the 0·47 power of the total pressure, and the activation energy is 12·3 kcal. A mechanism involving reaction between a chemisorbed and a physically-adsorbed molecule accords best with the observations for both reactions.

It is now generally accepted that the adsorption of unsaturated hydrocarbons on metal catalysts is of the associative type, that is, the double or triple bond is broken, and two covalent carbon-metal bonds are formed. This model has been successfully used [1, 2] to explain many of the features of their behaviour in hydrogenation reactions. One of the most compelling pieces of evidence for this mode of adsorption is the work of Conn and Twigg,[3] who found that there was no exchange between ethylene and tetradeutero-ethylene over a nickel catalyst in a wide range of temperature. If adsorption were of the dissociative type, the fragments H, D, C_2H_3 and C_2D_3 would result, and exchange would presumably occur by their random recombination.

Similar considerations would lead one to expect that there would be no exchange between acetylene and dideutero-acetylene; an examination of the reaction

$$C_2H_2 + C_2D_2 \rightleftharpoons 2C_2HD$$

was therefore undertaken, and contrary to expectation it has been found to proceed to equilibrium over a nickel catalyst at moderate temperatures. This paper reports the investigation of the kinetics of this reaction, and a determination and a calculation of its equilibrium constant. The exchange reaction between dideutero-acetylene and methylacetylene has also been studied and its kinetics determined.

EXPERIMENTAL

Dideutero-acetylene (C_2D_2) was prepared by the reaction of heavy water with calcium carbide;[4] yields of about 70 % (based on the heavy water) were obtained. Infra-red analysis (described later) showed that the products of four separate preparations contained 98·0-98·4 % C_2D_2, the remainder being mainly C_2HD, in the amount to be expected from the purity of the heavy water.

Other hydrocarbons were treated and used as described in earlier parts of this series. Nickel catalysts (2 g samples prepared as described in part 1 [5]) were used for all the exchange experiments.

The reaction system used has been described previously.[5] Preliminary infra-red analyses showed that two species in the reaction system could be conveniently estimated with pressures in the absorption cell of about 1 mm; a simple volume-sharing device was therefore constructed and calibrated, which enabled cell pressures to be measured with an accuracy of ± 0·02 mm. Catalyst samples, which had been initially reduced in hydrogen and tested for hydrogenation activity, were treated with about 200 mm of C_2H_2 at the reacting temperature for at least an hour before an exchange run was attempted; this was in order to remove any traces of hydrogen remaining on the surface after pumping. The C_2D_2 was added to the reaction vessel first in all cases. In order to ensure that samples were representative, a small volume of gas was normally rejected half a minute before each sample was taken.

INFRA-RED ANALYSIS.—The reactions were followed by measuring the changes in intensity of selected absorption bands in the infra-red region; the spectra were recorded by a Grubb-Parsons spectrometer with a rock-salt prism. The bands chosen were the *Q* branch of the C_2H_2 band at 729 cm^{-1}, the *Q* branch of the C_2HD band at 683 cm^{-1}, and the maximum of the unresolved *R* branch of the C_2D_2 band at 2427 cm^{-1}. This last is much weaker, and required higher pressures for its measurement. The calibration curves of $\log_{10}$ % transmission against pressure are shown in fig. 1, and refer to a cell 10 cm long, and to slits of 0·70, 1·10, 0·12 mm for C_2H_2, C_2HD and C_2D_2 respectively. The C_2H_2 curve was obtained with the pure gas, and correction was made for the trace of C_2HD in the C_2D_2. The C_2HD curve was constructed by using an equilibrium mixture in which the concentrations of C_2H_2 and C_2D_2 had been carefully determined. These curves were used for analysis directly. At low pressures of C_2H_2 and C_2HD, the measured intensity was sensitive to pressure-broadening effects, and in each case the pressure was made up to atmospheric by the introduction of air. No serious overlapping of bands occurred at the pressures employed, and correction was made for false or scattered radiation by means of a glass shutter. Analyses were reproducible to ± 2 % of the amount present, but in view of the indirect nature of the C_2HD calibration and the possible errors arising from pressure-broadening, the absolute accuracy may be better represented by ± 5 %.

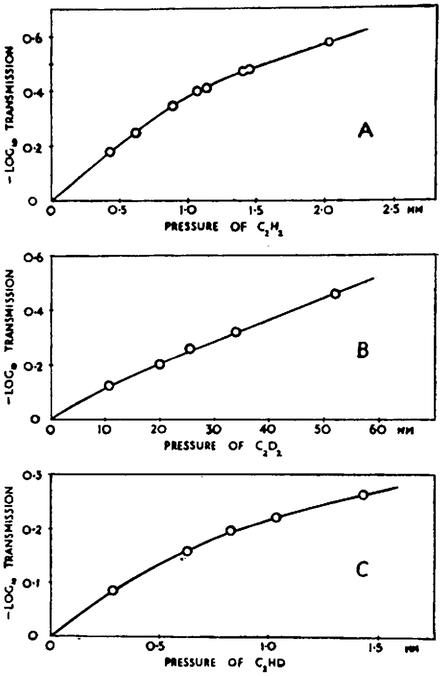


FIG. 1.—Calibration curves for the infra-red analysis of C_2H_2, C_2HD and C_2D_2.

RESULTS

THE EXCHANGE REACTION BETWEEN ACETYLENE AND DIDEUTERO-ACETYLENE.—*The course of reaction and measurement of the equilibrium constant.*—In a number of the first exchange runs, the course of the reaction was followed as fully as possible in order to check the methods of analysis. The results for a typical run are shown in fig. 2, where the percentage of C_2HD expected from C_2H_2 removed is plotted for comparison with the observed value. The full lines correspond to an exponential reaction with a half-life of about 27 min. Owing to the higher pressure required for estimating C_2D_2, its concentration could only be determined at the end of a run.

Standard C_2H_2 hydrogenation runs were performed before and after each of the first four exchange runs, in order to check that the catalyst activity was not modified by contact with the acetylenes. The results showed that prolonged treatment with the acetylenes caused no deactivation, but that hydrogenation runs caused the rate of the subsequent exchange experiments to decrease. For this reason, such standard hydrogenation runs were abandoned, and the rate of the exchange reaction under fixed conditions of partial pressure was adopted as the sole criterion of catalyst activity. It was found that if the catalyst were kept under C_2H_2 at the operating temperature, its activity was usually retained in a satisfactory manner.

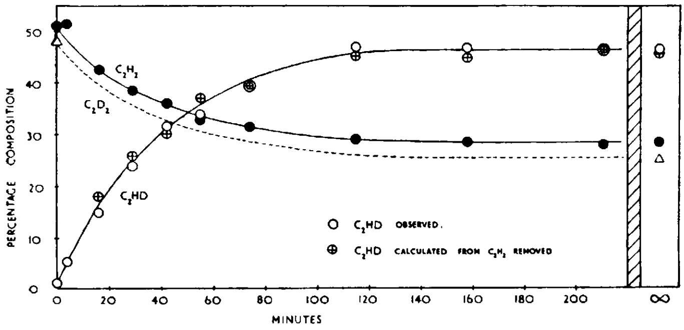


FIG. 2.—The course of the exchange reaction between C_2H_2 and C_2D_2 at 119° C; ○ C_2HD observed; ⊕ C_2HD calculated from C_2H_2 removed.

Over a new sample of catalyst the rate of exchange at 90° C was comparable with the rate of hydrogenation; it was also shown that no measurable exchange occurred in the absence of the catalyst. The concentrations of the three species at equilibrium were carefully determined in a number of cases, and the results are given in table 1.

TABLE 1.—THE DETERMINATION OF THE EQUILIBRIUM CONSTANT

run	T° C	initial composition %			final composition %			K
		C_2H_2	C_2HD	C_2D_2	C_2H_2	C_2HD	C_2D_2	
3	81	53·5	1·0	45·5	30·5	47·5	22·0	3·4
4	119	51·0	1·0	48·0	28·5	46·5	25·0	3·0
6	100	49·5	1·0	49·5	27·0	47·5	25·5	3·3
7	100	49·0	1·0	50·0	25·5	47·5	27·0	3·3
16	60	49·0	1·0	50·0	26·0	47·0	27·0	3·1
38	65	18·7	1·6	79·6	4·6	29·7	65·6	2·9
							mean =	3·2

If there were no heat of reaction, the equilibrium constant would be 4, corresponding to the statistically probable ratios of $C_2H_2/C_2HD/C_2D_2$ of 1/2/1. The experiments indicate a lower value, and the same conclusion is reached from a theoretical calculation. This calculation has already been performed by Glockler and Morrell,[6] but due to drastic revision of the vibration frequencies, a recalculation has become necessary. Using the fundamental frequencies as given by Herzberg,[7] the zero-point energy difference for the reaction is 27 cm^{-1}, that is, $E_0 = 77$ cal. The contribution to the free energy from the vibrational partition functions can be calculated from the tables of Wilson,[8] and an approximate value of the rotational contribution may be obtained using the moments of inertia of Herzberg, Patat and Spinks,[9] and the symmetry number 2 for both C_2H_2 and C_2D_2; this leads to the main factor of 4 in the equilibrium constant.

The final result is $K = 3{\cdot}58$ (350° K); and 3·62 (400° K) which may be expressed as a temperature independent value of 3·6 ± 0·3 in the range 80-130° C. The error arises from the uncertainty in two of the frequencies, as discussed by Herzberg, and also from the neglect of anharmonicity. The value is in reasonable agreement with the mean experimental value of 3·2 in the range 60-120° C. The experimental value also has a large margin of absolute error (estimated at ± 0·5) since its percentage inaccuracy is four times the possible error in determining each concentration.

The obvious rate equation to test is

$$d[C_2HD]/dt = k(3{\cdot}2[C_2H_2][C_2D_2] - [C_2HD]^2),$$

which expresses the fact that C_2HD formation occurs by a bimolecular reaction, and that it is destroyed by the reverse reaction of two C_2HD molecules with a rate constant 1/3·2 times that for the forward reaction. The net rate is therefore zero when all species have their equilibrium concentrations. If at time t the mole fraction of C_2HD is x, then the fractions of C_2H_2 and C_2D_2 will be $(1/2 - x/2)$ if each is initially 1/2. The rate equation then becomes

$$dx/dt = 3{\cdot}2k(1/2 - x/2)^2 - kx^2,$$

and its solution is

$$\left(1 - \frac{x}{0{\cdot}47}\right) = \left(1 + \frac{x}{8{\cdot}47}\right) \exp\left(-\,1{\cdot}788\, kt\right).$$

If the term $x/8{\cdot}47$ were constant, the reaction would be exponential, but since x varies only from 0 to 0·47 during the course of a reaction, the variation in this term is only ± 3 % which is within experimental error. The agreement of the full line with the points in fig. 2 can therefore be regarded as justification for the above rate expression, and the reaction will be treated as exponential in later sections. This pseudo-exponential character also occurs when the initial mole fractions are not each 1/2; an exactly exponential solution would, however, result from an equilibrium constant of 4.

The order of reaction.—The order of reaction with respect to total pressure at a constant 1/1 ratio of reactants was determined at 70° C; the results are shown in fig. 3. The rate is proportional to the power 0·65 of the total pressure. This form of pressure dependence suggests that an adsorption process (governed by the Langmuir isotherm) may be involved. The chemisorbed layer is thought to be saturated even at low pressures, but a change of pressure will certainly affect the concentration in any physically-adsorbed layer above it, in accordance with the isotherm. If exchange occurred between chemisorbed and physically-adsorbed molecules, the rate would be expected to depend on the concentration in the first physically-adsorbed layer, that is, on a fractional power of the pressure, as found.

The effect of temperature.—The effect of temperature on the rate of reaction was observed in the range 40-100° C with a constant total pressure of 152 mm and a 1/1 ratio of reactants. The plot of $\log_{10}$ initial rate against $1/T°$ K gives a good straight line of slope corresponding to an apparent activation energy of 10·7 ± 0·3 kcal.

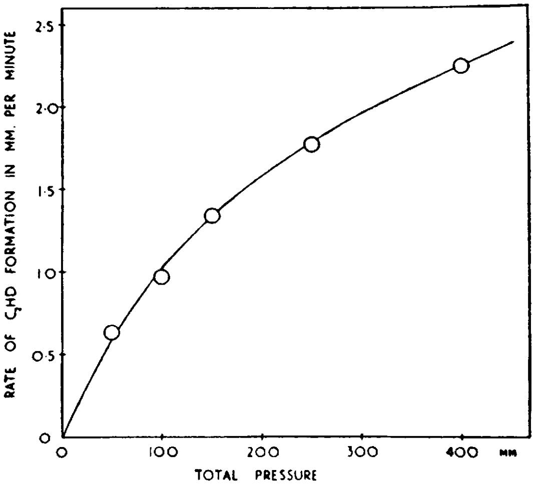


FIG. 3.—The order of reaction with respect to total pressure of the $C_2H_2+C_2D_2$ exchange reaction at 70° C.

The effect of varying the initial ratio of reactants.—Table 2 summarizes the results of some experiments in which the initial C_2H_2/C_2D_2 ratio was widely varied at constant total pressure. The position of half-reaction was calculated by assuming the mean value for the equilibrium constant reported earlier. The times of half-reaction are seen to be equal within experimental error. This constancy shows that the rate equation stated previously is satisfactory; in addition, it means that the concentrations in the surface layers are proportional to those in the gas phase, whereas preferential adsorption of either species would lead to a variation of the time of half-reaction with the initial ratio. Both C_2H_2 and C_2D_2 must therefore have similar strengths of adsorption.

TABLE 2.—THE EFFECT OF VARYING THE INITIAL RATIO OF REACTANTS AT TOTAL PRESSURE = 150 ± 2 mm

run	initial C_2H_2/C_2D_2 ratio	$t_{\frac{1}{2}}$ (min)
39	1·00	45½
40	5·07	43
41	0·22	45½
42	0·98	45½

THE EXCHANGE REACTION BETWEEN DIDEUTERO-ACETYLENE AND METHYLACETYLENE.—*The course of reaction and measurement of the equilibrium constants.*—This reaction was found to proceed at a rate comparable with the acetylene exchange; it was followed by observing the rate of formation of C_2HD and C_2H_2. It was first necessary to decide how many of the four hydrogen atoms in methylacetylene were exchanging, and assuming a statistical distribution (that is, ignoring zero-point effects) the expected equilibrium concentrations of the acetylenes were calculated for the two possible cases; these values, together with those observed in a typical experiment, are shown in table 3, and have been calculated for an initial composition of 50 % C_2D_2 and 50 % methylacetylene. These results make it certain that only one hydrogen atom is exchangeable; it is presumably that directly attached to the carbon triple-bond system.

Additional evidence strongly supporting this conclusion was obtained by an examination of the spectrum of the products in the range where absorption due to deuterium substitution in the methyl group would be expected (that is, in the range of the C—D stretching frequency in C_2D_6); no strong bands were detected.

TABLE 3.—CALCULATED AND OBSERVED EQUILIBRIUM CONCENTRATIONS

	% C_2H_2	% C_2HD	% C_2D_2
assuming 1 hydrogen exchanges	5·5	22·2	22·2
assuming 4 hydrogens exchange	22·2	22·2	5·5
observed	5·8	19·7	23·0

A new strong band was observed at 2605 ± 10 cm^{-1}, and this was attributed to the C—D stretching frequency in CH_3CCD. This may be compared with the corresponding frequency in C_2HD, which is 2584 cm^{-1}. The deuterium exchanged by C_2D_2 is therefore present as $CH_3—C{\equiv}C—D$ (methyl-deutero-acetylene, hereafter written as CH_3CCD) and the course of reaction can now be fully analyzed. C_2D_2 can be estimated by difference of the acetylene pressures, and the deuterium lost from the acetylenes gives the amount of CH_3CCD present; methylacetylene can then also be found by difference. The course of a typical reaction is shown in fig. 4.

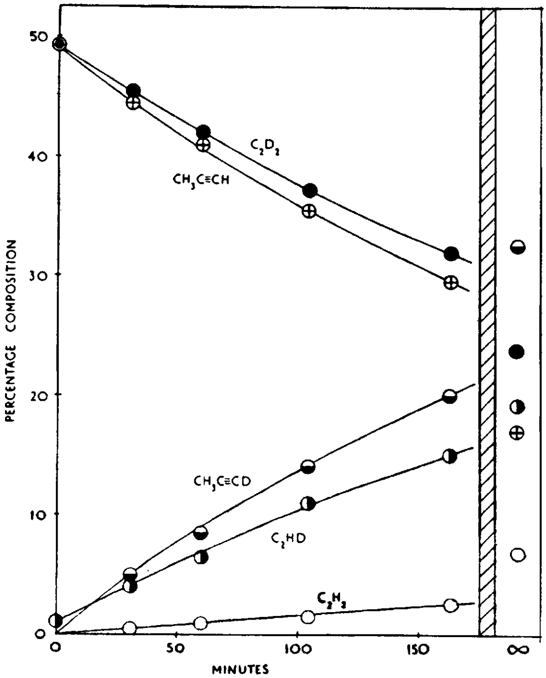


FIG. 4.—The course of the exchange reaction between C_2D_2 and methylacetylene at 62° C.

The reactions producing exchange are therefore

$$C_2D_2 + CH_3CCH \rightleftharpoons C_2HD + CH_3CCD \qquad K_1$$
$$C_2HD + CH_3CCH \rightleftharpoons C_2H_2 + CH_3CCD \qquad K_2$$
$$2C_2HD \rightleftharpoons C_2H_2 + C_2D_2 \qquad 1/K$$

This system offers an immediate explanation of the course of reaction. CH_3CCD is formed faster than C_2HD, and methylacetylene is removed faster than C_2D_2 because the second reaction begins to assert itself as soon as any C_2HD is formed. The concentrations of the reactants and products at equilibrium were determined in several cases, and the results are given in table 4. Because of zero-point effects, K_1 and K_2 differ somewhat from the statistical values of 2 and 1/2 assumed in constructing table 3. The complete set of fundamental frequencies of CH_3CCD which is required for calculation of K_1 and K_2 is not available. The mean value of K ($= K_1/K_2$) agrees well with that obtained from table 1.

TABLE 4.—EQUILIBRIUM CONCENTRATIONS OF REACTANTS AND PRODUCTS

run	initial composition %			final composition %					K_1	K_2	$K = \frac{K_1}{K_2}$
	CH_3CCH	C_2HD	C_2D_2	C_2H_2	C_2HD	C_2D_2	CH_3CCH	CH_3CCD			
33	51·8	1·0	47·2	5·8	19·7	23·0	22·1	29·7	1·2	0·40	2·9
62	49·5	1·0	49·5	5·3	20·4	24·8	19·5	30·0	1·3	0·40	3·2
74	51·0	0·8	48·2	5·9	19·9	23·2	20·1	30·9	1·3	0·45	2·9
										mean =	3·0

The order of reaction.—The order of reaction with respect to total pressure at a constant 1/1 ratio of reactants was determined at 99° C. The results are presented in fig. 5. The rate is proportional to the power 0·47 of the pressure; this is very similar to the pressure dependence of the exchange reaction with acetylene, and strongly suggests that the same type of mechanism is operative.

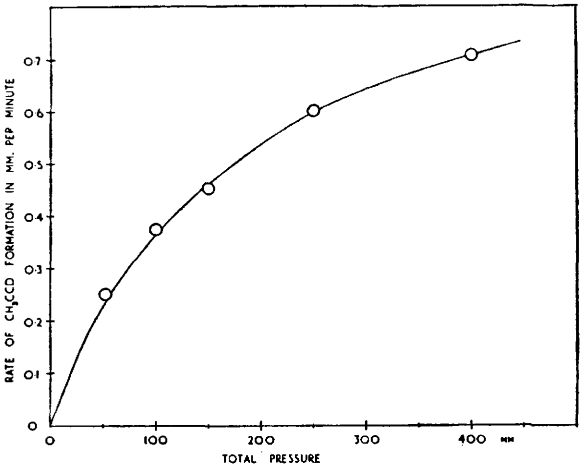


FIG. 5.—The order of reaction with respect to total pressure of the C_2D_2-methylacetylene exchange reaction, at 99° C.

The effect of temperature.—The effect of temperature on the rate of formation of CH_3CCD was examined in the range 74-133° C with a constant total pressure of 153 mm and a 1/1 ratio of reactants. The plot of $\log_{10}$ initial rate against $1/T°$ K gives a good straight line of slope corresponding to an apparent activation energy of 12·5 ± 0·3 kcal.

The effect of varying the initial ratio of reactants.—Table 5 summarizes the results of experiments in which the initial ratio of reactants was widely varied at constant total pressure. Relative rates of reaction were obtained by averaging the rate over the first 1/6th of the reaction; this procedure was sounder than measuring initial rates, since it

TABLE 5.—THE EFFECT OF VARYING THE INITIAL RATIO OF REACTANTS

run	ratio CH_3CCH/C_2D_2	relative rate	product of mole fractions	$\frac{\text{relative rate}}{\text{product of mole fractions}}$
59	1·06	1·0	0·250	0·512
60	0·18	0·42	0·127	0·425
61	5·30	0·63	0·134	0·610

placed reliance on more experimental points. If methylacetylene and C_2D_2 were equally strongly adsorbed, so that the fractional surface coverages were proportional to their mole fractions in the gas phase, the rate would then be proportional to the product $[CH_3CCH][C_2D_2]$. The last column should therefore be constant, and the fact that it is clearly not so is taken to indicate that both reactants are not equally strongly adsorbed.

In general,

$$\theta_2/\theta_3 = kx_2/x_3,$$

where θ represents the fractional coverage in the chemisorbed layer, x the mole fraction of the reactant, k a constant (equal to unity for equal strengths of adsorption), and where the subscripts 2 and 3 refer to C_2D_2 and methylacetylene respectively. Furthermore

$$\phi_2/\phi_3 = k'x_2/x_3,$$

where ϕ_2 represents the fraction of the physically-adsorbed layer occupied by C_2D_2 and ϕ_3 that by C_3H_4, and k' another constant; the other symbols have their former significance. Making use of the reaction model proposed earlier (that is, reaction between a chemisorbed and a physically-adsorbed molecule), it may be assumed that

$$\text{rate of reaction} = A\theta_2\phi_3 + B\theta_3\phi_2.$$

By simple algebra, remembering $\theta_2 + \theta_3 = 1 = \phi_2 + \phi_3$, this is equal to

$$\frac{(Ak + Bk')x_2x_3}{x_3^2 + x_2x_3(k + k') + x_2^2kk'},$$

and the relative rates divided by x_2x_3 vary as

$$[x_3^2 + x_2x_3(k + k') + x_2^2kk']^{-1}.$$

From the relative rates in table 5, k and k' have been evaluated; it is found that

$$k = 1\cdot1 \quad \text{and} \quad k' = 1\cdot5,$$

$$\text{or} \quad k = 1\cdot5 \quad \text{and} \quad k' = 1\cdot1.$$

This treatment cannot distinguish between k and k', but it is likely that direct proportionality to the pressure ratio will be approached in the physically-adsorbed layer, that is, $k' \simeq 1$. This leaves the 1·5 value for the " chemisorbed-layer constant ", which is in good agreement with hydrogenation studies.[10]

THE EXCHANGE OF DIDEUTERO-ACETYLENE WITH OTHER UNSATURATED HYDROCARBONS.—Under conditions where there was a rapid reaction between acetylene and C_2D_2, there was no measurable exchange between C_2D_2 and allene, or between C_2D_2 and ethylene, during periods of several hours.

DISCUSSION

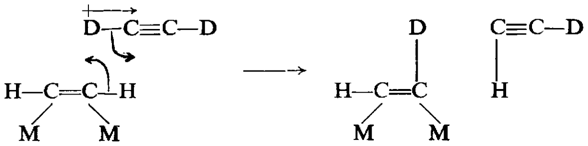
The occurrence of exchange reactions of this type was not predicted on the basis of existing theories of hydrocarbon adsorption, and so it might seem to be necessary to postulate dissociative adsorption of the acetylenes. However, a closer examination of the relevant data shows that this may not be so.

The dissociation of acetylene into C_2H and H fragments would infer a large concentration of atomic hydrogen, but the evidence is against this; for example, the kinetics of acetylene hydrogenation [2] show that the reacting hydrogen is not chemisorbed, and furthermore the conversion of para-hydrogen is inhibited by acetylene even more strongly than by ethylene.[11] Moreover the presence of C_2H and H fragments on the surface would almost certainly initiate hydrogenation and polymerization reactions, whereas the maintenance of catalyst activity over a set of exchange reactions suggest that when acetylene is adsorbed alone over nickel no irreversible changes take place. There seems to be no good case for advocating the dissociative adsorption of acetylene while retaining the associative mechanism for ethylene; the C—H bond is probably stronger in acetylene than in ethylene,[12] and hence it would be difficult to explain the preferential adsorption of acetylene in the presence of ethylene on this basis. It can, however, be readily explained in terms of the associative adsorption of these hydrocarbons.[2, 10]

It is therefore necessary to seek some other point of difference between acetylene and ethylene in order to explain their differing behaviour in exchange reactions.

It is suggested that the source of reactivity in acetylene is the polar nature of the C—H link, in which the hydrogen atom is more positive than in the majority of hydrocarbons. Chemical evidence shows that an acetylenic hydrogen atom has marked acidic properties. Definite evidence concerning the magnitude of the polarity is not available, but Gent[13] has suggested that in saturated hydrocarbons the dipole is $\overset{+\!\!\longrightarrow}{\mathrm{C{-}H}}$, that ethylenic C—H bonds have no dipole, and that acetylenic C—H bonds are polarized as $\overset{\longleftarrow\!\!+}{\mathrm{C{-}H}}$.

The reaction might therefore be represented diagrammatically as follows (M represents a catalyst atom):



where the C_2D_2 molecule is physically-adsorbed and the C_2H_2 chemisorbed.

It has already been noted that such a mechanism is in accordance with the observed order of reaction, provided that the coverage of available sites for physical adsorption is not close to zero or unity. It has been found useful to propose physical adsorption of hydrocarbon molecules to explain some of the features of the hydrogenation of methylacetylene and allene.[5, 14] Generally speaking, however, the amount of physically-adsorbed acetylene over a fully chemisorbed layer would not be expected to be large at these temperatures. It may therefore be that a certain number of sites are available with a rather larger energy of adsorption; such sites could be above vacant nickel atoms, of which there would be about 12 % according to statistical estimation.[2]

This mechanism also explains readily why only the acetylenic hydrogen in methylacetylene is exchangeable with C_2D_2; it may also explain the absence of a similar exchange reaction between ethylene and C_2D_4, where the C—H bonds are not sufficiently polar to enable reaction to take place. The absence of exchange between C_2D_2 and ethylene, and C_2D_2 and allene could be explained on similar lines.

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