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Acetylene Deuteration in the Presence of [^{14}C]Ethylene

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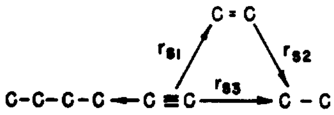
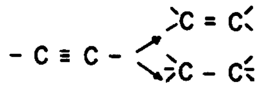
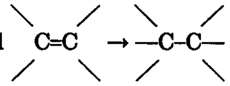
The selective deuteration of 2.1 kN m^{-2} of a mixture containing 90% acetylene and 10% [^{14}C]ethylene in the presence of 8.4 kN m^{-2} deuterium gas was studied at 273 and 303 K over Pd black catalyst. Product samples were separated by gc and the column effluent was analyzed by quantity, radioactivity, and deuterium contents of the individual peaks. The double labeling method related surface reaction steps and the adsorption/desorption properties of intermediate at the *same activity level* of the catalyst. Thus, disparities resulting from studies of these parameters in separate experiments were eliminated. The observed overall reaction network in the adsorbed phase is



Ethylene desorption was fast compared to its further reaction and its readsorption occurred only when the amount of acetylene decreased below a certain level. Initially acetylene monopolized the site, and the sole process was



Subsequently, after acetylene partial pressure diminished, ethylene could competitively adsorb, and



occurred.

INTRODUCTION

Reactions having zero order dependence with respect to one or more reactants are of considerable scientific and industrial importance. Commercial applications are selective hydrogenation of trace acetylene in ethylene and dienes to mono-olefins.

Early work on acetylene hydrogenation and on deuterium exchange has been reviewed by Bond (*1–3*). In these studies supported palladium, among transition metals in Group VIII, was found to be the most effective catalyst in the selective formation of ethylene. Furthermore, it has been established that selectivity in reactions containing acetylene as sole reactant increased with increasing pressure of acetylene and with temperature; and there was

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inverse dependence on hydrogen pressure. Ethylene formation has been discussed in terms of thermodynamic and mechanistic selectivity, the former taking into account the difference in strength of adsorption between acetylene and ethylene, the latter being responsible for the parallel reactions of acetylene to ethylene and ethane.

The behavior described in these studies holds when the initial reaction mixture contains large amounts of ethylene (*4*). However, experiments by McGown *et al.* using ^{13}C-labeled acetylene and deuterium in place of hydrogen showed that in the initial stage of reaction ethylene does not act as inert diluent but does participate in the reaction (*5*). The resulting selectivity, however, is not thermodynamic in nature since the change in the partial pressure does not affect the selectivity. It was, therefore, assumed that this behavior indicated that two types of sites existed, one that hydrogenated ethylene in the presence of acetylene and one on which the hydrogenation of acetylene and ethylene proceeded together.

Selectivity depends on the aging of catalysts. On peripherally deposited Pd catalyst (*4*) activity for acetylene hydrogenation increased and selectivity decreased after 750 hr reaction time. The same effect was found by McGown *et al.* (*5*) where on fresh catalyst $S \sim 20$, while on aged Pd this value decreased down to 2–3. This change may be due to the formation of β-Pd-H phase which is active in, e.g., ethylene hydrogenation (*6*). Recent work (*7, 8*) indicates that, with the formation of β-Pd-H phase, acetylene hydrogenation activity increases with the simultaneous decrease in selectivity, thus the slow build-up of a β-Pd hydride phase may be in correlation with aging.

In addition, it may be assumed that decrease in selectivity for ethylene formation on aging is caused by a change in adsorption–desorption properties of intermediate. Similar phenomenon were demonstrated in the hydrogenation of ethylene using nonsupported metal catalyst in the presence of tritiated hydrogen (*9, 10*). At high hydrogenation activity the rate of hydrogenation of adsorbed ethylene surpassed that of ethylene desorption and so tritiated ethylene in the gas phase could not be found. On aging, when hydrogenation activity decreased and thus adsorption/desorption equilibrium for ethylene was attained, tritiated ethylene could be monitored in the gas phase. The same behavior was found for cyclohexane conversion in the presence of deuterium (*11*).

In studying a reaction, such as, in this case, selective hydrogenation, it is extremely important that all information about the elementary steps that lead to the formation of intermediate and product, as well as the rate of surface reactions, etc., should be obtained at constant catalyst activity. In practice, it is nearly impossible to hold this condition because such data usually are obtained only in separate reactions or serial measurements. To avoid this we apply here a double labeling method using ^{14}C-labeled ethylene and deuterium gas simultaneously, to investigate the surface reaction path in the deuteration of unlabeled acetylene.

EXPERIMENTAL

The experimental setup used for the double-labeling study is shown in Fig. 1. An all-glass circulating batch reactor was used for deuteration. The volume of the reaction system is 130 ml, and the gas mixture was circulated at 300 ml/min. A six-way sampling valve was used to withdraw a small fraction of the reacting mixture for analysis. The mixture was then separated chromatographically on a Perkin-Elmer Model 900 gc and quantitatively analyzed by a flame ionization detector. After the column, but before entering the detector, the gas stream was dynamically split. About 9/10 of the amount was passed through a Nuclear-Chicago Tracerlab Versamatic V Scaler Model D-47 proportional flow counter to measure the radioactivities of the different components. The remaining $\frac{1}{10}$ portion was again split, one portion to the FID and the other to a DuPont 21-491 double-focusing mass spectrometer for analysis of deuterium content of the individual compounds. Hydrogen content in deuterium gas cannot be measured by this type of mass spectrometer. Details for the apparatus can also be found elsewhere (*10*).

The reaction products were separated on a 2′ × $\frac{1}{8}$″ stainless-steel chromatographic column packed with γ-alumina, temperature programmed from 40 to 140°C (26°C/min).

The constancy over the course of a 35-min experiment of the split ratio was assumed, but not measured, in the experiments reported here. Diffusion in the lines to and in the counter itself caused peak broadening and consequent radioactivity measurement inaccuracies. Refinement of the experimental technique and the calculation of rate constants will be the subject of future work.

Deuterium gas was purified by passing through a silver-palladium thimble, [^{14}C]-ethylene was supplied by New England Nuclear Company with a specific radioactivity of 9.0 mCi/m*M*, and was diluted with nonradioactive ethylene before use to an extent required by the experiments. Approximately 20 mg Pd black catalyst (Strem Chemical, Inc.) was used in one experiment. The Pd black was reduced in 13.3 kN m^{-2} H_2 for 1 hr at 623 K and then evacuated for 1 hr at 623 K prior to gas admission. The specific surface area was 3.71 m^2/g with an average particle size of ~350 Å. The reaction mixture composition initially was 8.4 kN m^{-2} deuterium and 2.1 kN m^{-2} of a mixture containing 90% C_2H_2 and 10% [^{14}C]C_2H_4. Gases were premixed and then admitted to the catalyst. After each run the catalyst was evacuated for 1 hr. Activity decay was not measurable.

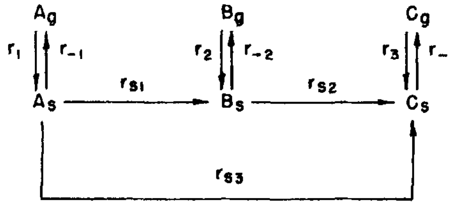
The calculation of specific radioactivity for each product was determined by the integrated counts (area of the radioactive peaks) diminished by the background and divided by the pressure in m*M* of that substance. Due to the errors inherent, in determination of radioactivity, especially at low pressures of ethylene, the total radioactivity curve was first smoothed and then divided by the corresponding quantity in m*M*.

Mass spectra of each compound were determined at 70 V electron accelerating voltage. In the calculations the spectra were corrected for naturally occurring ^{13}C and for fragmentation.

RESULTS

Principle of Double-Labeling Method

Selective hydrogenation (or deuteration) of trace acetylene to ethylene and dienes to mono-olefins can be represented by Scheme I:



(I)

where A_g, B_g, and C_g are the gas phase concentrations of the reactant acetylene, intermediate ethylene, and final product ethane, A_s, B_s, and C_s are the corresponding surface concentrations, and r_n, r_{-n}, and r_{sn} are rates of adsorption, desorption, and surface reaction, respectively. Acetylene desorption and ethane readsorption are negligible in this case, and so r_{-1} and r_3 are very very small.

Considering the above scheme our task is to establish whether a direct route r_{s3} from A_s to C_s exists. If not, there is the possibility that the ethylene partial pressure will not change in the consecutive mechanism (represented by r_{s1} and r_{s2}) if there are comparable magnitudes for rates r_{-2} and r_{s2}.

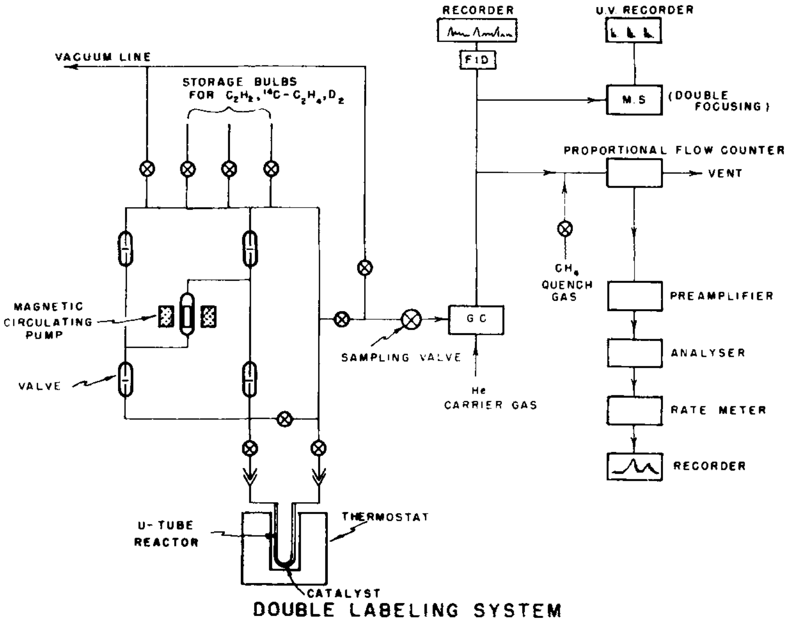


FIG. 1. Double-labeling system. Samples containing deuterium and ^{14}C from the recirculation reactor are resolved by gc, then split to FID, MS, and counting.

Use of ^{14}C-labeled A_g, (A^*_g). When A^*_g and B_g are used the difference in specific radioactivities (β, calculated in Ci/mol or equivalent unit) $\beta_{C_g} > \beta_{B_g}$ is indicative of the existence or r_{s3} only if adsorption/desorption equilibrium for intermediate, B_g, is proved.

Use of ^{14}C-labeled B_g (B^*_g). In the presence of B^*_g similar considerations are valid. Nevertheless, more information can be derived because when adsorption/desorption equilibrium for species B is not established the rate of decrease in β_{B_g} is a measure for r_{-2} since β_{B_g} is not changed by the readsorption of B_g.

We may overcome the difficulties presented above if all experiments are carried out in presence of deuterium instead of hydrogen. The simultaneous monitoring of deuterium substitution in A_g and B_g gives data on the adsorption/desorption properties of the reactant and intermediate. These experiments must be carried out simultaneously because the result of using these isotopes in subsequent runs is not unambiguous due to the change in the activity level of the catalyst.

Table 1 lists the information that can be obtained in one batch experiment utilizing [^{14}C]ethylene, unlabeled acetylene, and deuterium gas.

Acetylene Deuteration

Acetylene deuteration was carried out in presence of 10% [^{14}C]ethylene. The amounts of reactant and products vs time are plotted in Fig. 2 for both 273 and 303 K. The rate of acetylene disappearance of course increases with temperature, as well as the rates of ethylene and ethane formation.[3] Butane is gradually formed during the course of the reaction, but it does seem to be an initial product. The formation of ethane at the beginning of the reaction is slow and then a rapid reaction takes place.

[3] Species will be referred to generically as acetylene, ethylene, ethane, and butane, whether they contain deuterium or not.

TABLE 1

Rate Information That Can Be Derived from Double-Labeling Experiments[a]

	Symbols: β_B, β_C are the specific radioactivities of intermediates and products, respectively; r_2, r_{-2}, r_{s1}, r_{s2} and r_{s3} are given in reaction scheme	$\beta_B = f(t)$			
		β_B constant		β_B decreases	
		$\beta_B/\beta_C = 1$	$\beta_B/\beta_C > 1$	$\beta_B/\beta_C = 1$	$\beta_B/\beta_C > 1$
Deuterium Exchange in Intermediates		adsorption/desorption equilibrium: $r_2 = r_{-2}$			
	fast	$r_{s1} = 0$ $r_{s2} > 0$ $r_{s3} = 0$ impossible because there is reaction	$r_{s1} = 0$ $r_{s2} > 0$ $r_{s3} > 0$	$r_{s1} > 0$ $r_{s2} \ll r_{-2}$ $r_{s3} = 0$	$r_{s1} > 0$ $r_{s2} \ll r_{-2}$ $r_{s3} > 0$
		non-equilibrium adsorption/desorption: $r_2 > r_{-2}$			
	slow	$r_{s1} = 0$ $r_{s2} > 0$ $r_{s3} = 0$ impossible	$r_{s1} = 0$ $r_{s2} > 0$ $r_{s3} > 0$ or $r_{s1}/r_{-2} \cong 1$ are indistinguishable	$r_{s1} > 0$ $r_{s2} \cong r_{-2}$ $r_{s3} = 0$	$r_{s1} > 0$ $r_{s2} \cong r_{-2}$ r_{s3} is undefined

[a] β_B, β_C are the specific radioactivities of intermediates and products, respectively; r_2, r_{-2}, r_{s1}, r_{s2}, and r_{s3} are given in reaction scheme.

The reaction was also followed by the change of radioactivity of the different species. The specific radioactivity of ethylene was determined before starting the reaction.

Acetylene and butane did not show significant radioactivity, only ethylene and ethane were radioactive. Figure 3 shows the change in specific radioactivity of ethylene and ethane with time at 273 and 303 K, respectively. Initially there is a sharp drop in ethylene radioactivity as a consequence of hydrogenation of unlabeled acetylene. More importantly, ethane activity extrapolates to zero at low conversion, and is always lower than that of ethylene, suggesting that the ethane is, at least initially, formed from acetylene without intermediate desorption. Figure 4 gives the distribution of the different deuterated ethylenes at 273 and 303 K. Figure 5 gives the analogous plot for the different deuterated ethanes. As expected, the dominant species in ethylene is dideuterated $C_2H_2D_2$ while the other species together do not exceed 20%. $C_2H_2D_2$ is the initial product, and exchange reactions are slower than selective hydrogenation. Initially $C_2H_4D_2$ and $C_2H_2D_4$ are the main components in the ethanes mixture at the beginning of the reaction, i.e., in the first 12 min at 273 K and 1.5 min at 303 K. The decrease in $C_2H_4D_2$ concentration by exchange reactions is accompanied by an increase in $C_2H_2D_4$ and other deuterated species. These become dominant with the course of the reaction. The data on Fig. 5 at 303 K also confirm that $C_2H_2D_4$ is an initial reaction product.

DISCUSSION

As seen in Fig. 2 the main route of the reaction is the consecutive deuteration of acetylene to ethylene and then to ethane. This is obvious from the maxima in the

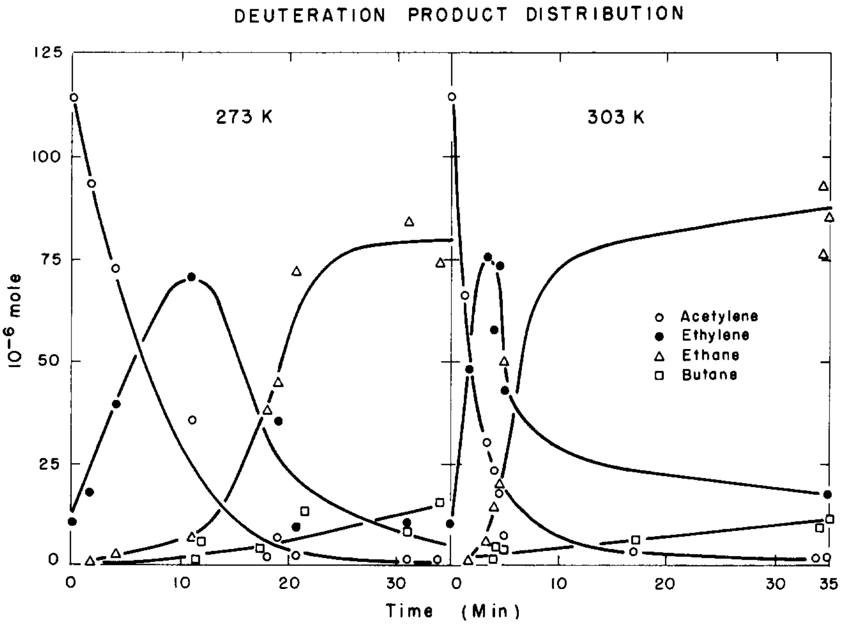


FIG. 2. Amounts (in mole) of acetylene, ethylene, ethane, and butane, at 273 and 303 K.

amounts of ethylene formed. In addition to the consecutive pathway, part of the ethane is formed via a concerted mechanism, shown by the positive initial slope of the ethane pressure vs time curve.

The crucial problem is to ascertain

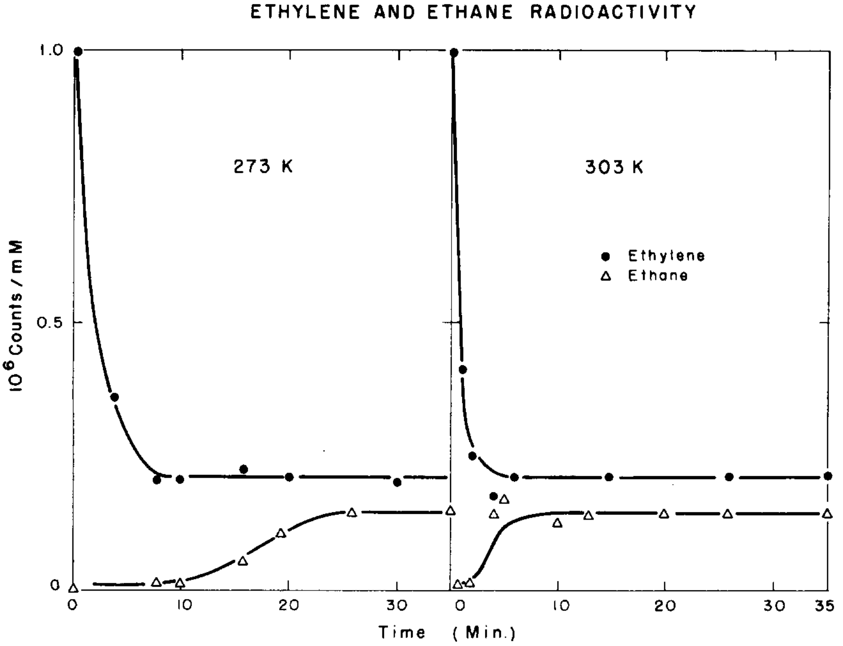


FIG. 3. The specific radioactivity (counts/mM) of labeled ethylene and ethane.

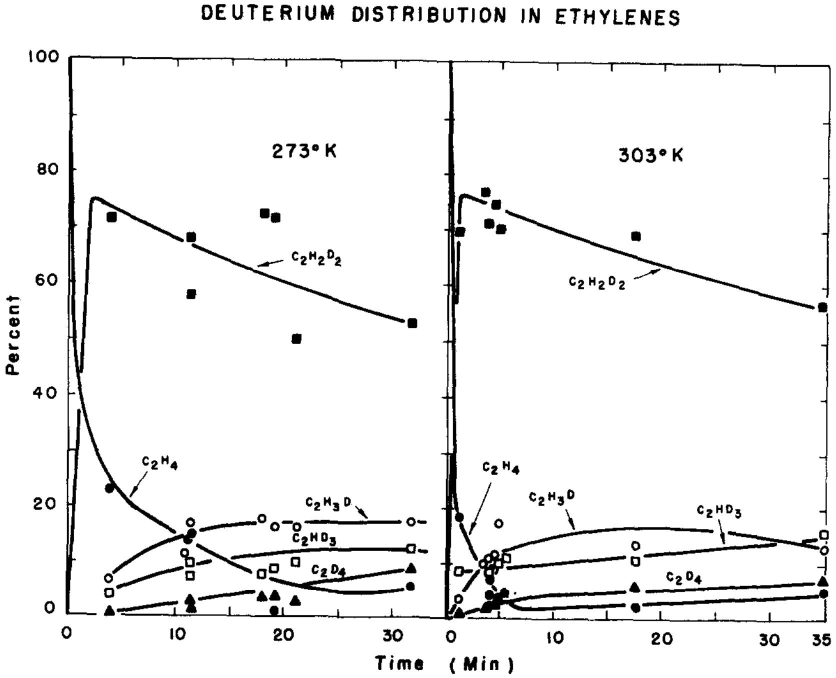


FIG. 4. Percentage deuterium distribution in ethylene at 273 and 303 K.

whether the ethane initially formed came from acetylene only via the concerted pathway. If so, ethylene can be considered an inert diluent when a large amount of acetylene is present (*12*). Alternatively, acetylene and ethylene deuteration take place simultaneously, as reported by McGown *et al.* (*5*).

By analyzing the ^{14}C-tracer data it is clearly seen (Fig. 4) that initially there is

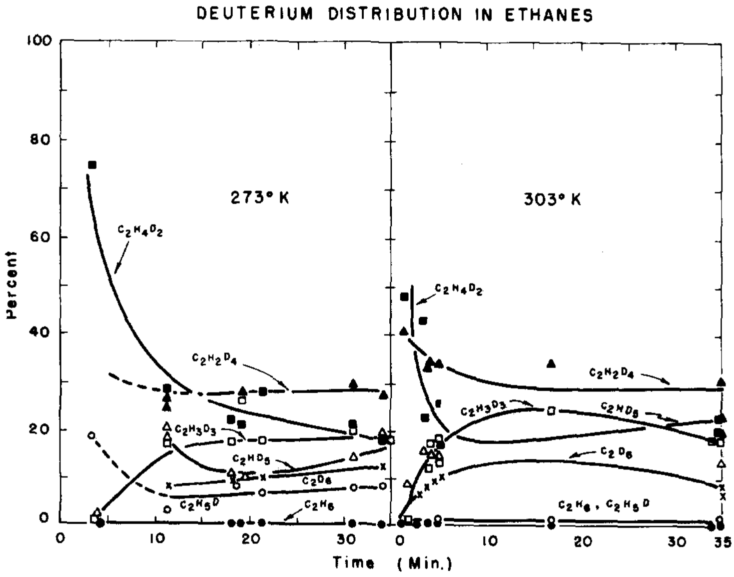


FIG. 5. Percentage deuterium distribution in ethane at 273 and 303 K.

a large drop in specific radioactivity of ethylene, which is a result of the unlabeled acetylene → ethylene reaction. By comparing the specific radioactivities of ethylene and ethane it is seen that the last column in Table 1 is operative. Although ethane becomes radioactive as the reaction proceeds, the data show that the main route for ethane formation initially is the one directly from acetylene. The confirmations are as follows:

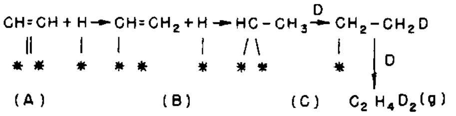
(i) The ratio of rates of acetylene consumption at two temperatures is nearly equal to the values obtained from the decrease of ethylene specific radioactivities. Accordingly, $r_{\beta\ \mathrm{ethylene}}\ (303)/r_{\beta\ \mathrm{ethylene}}\ (273)$ and $r_{\mathrm{acetylene}}\ (303)/r_{\mathrm{acetylene}}\ (273)$ are 3.33 and 2.93, respectively. In the decrease of specific radioactivity of ethylene all steps before B_g in Scheme I (r_1, r_{s1}, r_{-2}) are involved. In the disappearance of acetylene only r_1, r_{s3}, and r_{s1} are included (r_{s2} can be neglected initially). Ethylene desorption is not the fastest rate step, since the specific radioactivity of the ethane is smaller than that of ethylene. These data demonstrate that the initially direct route of unlabeled acetylene → unlabeled ethane proceeds exclusively initially, subsequently in addition to the deuteration of ethylene.

(ii) Acetylene adsorption is highly irreversible: This statement results from the nearly complete lack of deuterium exchange in acetylene, ($r_1 \gg r_{-1}$). This is opposite to results fround by McGown *et al.* (*5*).

This is also supported by the deuterium content of ethylene at the beginning. If acetylene adsorption should be completely associative we would have expected exclusively $C_2H_2D_2$. The existence of C_2H_3D as well as the substantial amounts of $C_2H_2D_2$, however, indicates a dissociation of acetylene-producing hydrogen atoms and acetylene residues strongly chemisorbed on the surface. Exchange of acetylene in the adsorbed phase would result in a considerable amount of C_2HD_3 and C_2D_4. Corollary to this, ethylene-d_1 points to the high concentration of H atoms on the surface (perhaps in the form of palladium hydride) which are partially used for hydrogenation of acetylene. Acetylene residues strongly bonded to the catalyst are dimerized to form nonradioactive butanes. The high amount of deuterium in the butanes indicates that during the formation of the C_4 fraction substantial exchange occurs on the surface.

(iii) The exchange of ethylene is not characteristic of the requirements shown in Table 1. This is because there is only slow ethylene exchange while acetylene is present in the system. Only when the major part of the acetylene has been used up does—besides fast ethylene hydrogenation—rapid ethylene exchange also take place. This is illustrated in Fig. 4 by the change of deuterium distribution at the second stage of reaction (after the initial acetylene deuteration).

(iv) By analyzing the deuterium distribution of ethane in the course of the reaction further confirmation is given for the direct route of deutero-ethane formation. At both temperatures the initial deuterated ethane is mainly ethane-d_2. At a later stage, the beginning of which coincides with the consumption of considerable acetylene, highly deuterated ethanes also appear. This phenomenon may give information about the pathway to directly formed ethane from acetylene. Analogous to Oliver and Wells (*13*), the following pathway on Pd can be considered:



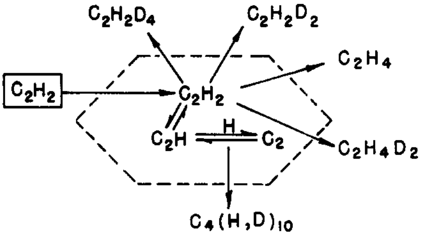
(II)

$\overset{\mathrm{H}}{\underset{*}{|}}$ in our case is initially present partly due to the presence of palladium hydride and partly from the dissociation of acetylene.

The uptake of two deuterium atoms produces ethane-d_2. Of course, later when acetylene is not present in the system the scrambling of D and H atoms in ethylene on the surface commences and thus the relative proportion of ethane-d_2 is promptly diminished.

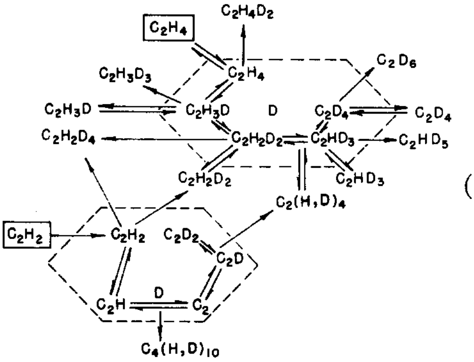
By comparing the deuterium distributions in ethane and ethylene at advanced stages of the batch reaction we may conclude that ethylene hydrogenation is faster than deuterium exchange, i.e., the surface species with deuterium scrambled is preferentially hydrogenated into ethane than desorbed to produce deuterated ethylene. The final conclusion is as follows:

The primary process involves monopolization of all of the catalytic sites by the 90% acetylene in the gas mixture [see Scheme (III)]:



(III)

Since the Pd may contain H atoms available for hydrogenation C_2H_4 is produced at the starting instants, as well as $C_2H_2D_2$. Radioactive ethylene in the gas phase does not adsorb at the strating instant, as evidenced by the lack of radioactivity in the initially produced ethane. This supports the observations by others that ethylene does not react on a surface until the acetylene is removed, at least for this situation where the reaction starts with 90% acetylene–10% ethylene mixture. In industrial selective hydrogenation, e.g., 0.35% acetylene in ethylene, there is not enough acetylene present to monopolize the surface, and so ethylene adsorbs competitively with acetylene. This is illustrated in Scheme (IV) where only some of the sites are occupied by acetylene, and the remainder are occupied by ethylene.

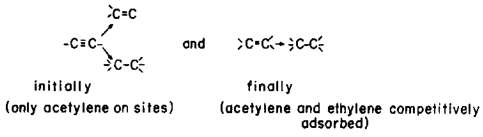


(IV)

It also represents in our present batch experimentation the situation where sufficient time has passed to reduce the amount of acetylene in the system and so make sites available also for ethylene adsorption. Also, by this time adsorbed H atoms from the Pd pretreatment are replaced by D atoms, and exchange reactions are noted on the scheme.

The important point to realize is that the acetylene reactions proceed on sites occupied by acetylene to produce both ethylenes and ethanes, just as in the start of the reaction, where there were only sites occupied by acetylene. As acetylene disappears to a sufficient extent, sites become competitively occupied by ethylene, and these react in their own fashion, to put exchanged ethylenes by adsorption/desorption into the gas stream and to surface deuterate these to the ethanes, which desorb irreversibly.

The "acetylene" sites and the "ethylene" are connected, so to speak, by the desorption of ethylenes from the former and the adsorption of those ethylenes on to the latter. Thus, the acetylene deuteration system is really two independent processes proceeding simultaneously, and only because of the readsorption of the ethylenes does it appear to be consecutive. From the point of view of the active sites, selective deuteration of acetylene should be represented as



SUMMARY

The double-labeling method, using both a radioactive ^{14}C-tracer and deuterium gas clearly demonstrated the reaction behavior involved in acetylene hydrogenation over Pd. This demonstration involved use of a static system, an interfaced GS–MS, and splitting the effluent from a gc column into three streams for analysis, radioactivity measurement, and deuterium distribution. The method is cumbersome to operate, but to compensate, the results are all obtained at the same state of catalyst surface, precluding the possibility of a system difference resulting in the change in the ratio of different surface reactions.

We are able to explain that on the Pd black catalyst we used for the hydrogenation of ethylene and of acetylene, results could be rationalized by one type of site. The ethane formed initially is a result of a parallel reaction of acetylene to ethane and ethylene. With the labeling technique it was unambiguously established that the rate of ethylene desorption is much faster than its further reaction on the surface to form ethane. Thus r_{s3} does exist. Further experimentation using CO poisoning, such as that described by McGown *et al.* (*5*, *14*), or adsorption measurements, described by Al-Ammar *et al.* (*15*), might well elucidate some fraction of a second type of site. However, McGown *et al.* have shown that the second type of site, on which both acetylene and ethylene hydrogenate simultaneously, does not operate when there is a large excess of acetylene. This is the situation we describe.

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