JOURNAL OF CATALYSIS 51, 173–184 (1978)

Hydrogenation of Acetylene in Excess Ethylene on an Alumina-Supported Palladium Catalyst at Atmospheric Pressure in a Spinning Basket Reactor

WILLIAM T. MCGOWN, CHARLES KEMBALL, AND DAVID A. WHAN

Department of Chemistry, University of Edinburgh, West Mains Road,
Edinburgh, EH9 3JJ, Scotland

Received May 30, 1977

The hydrogenation of acetylene in the presence of ethylene and carbon monoxide has been investigated in a spinning-basket reactor on a commercial supported palladium catalyst. The rate of disappearance of acetylene was found to be controlled by pore diffusion at low acetylene concentrations and was independent of acetylene at high acetylene pressures. In the non-diffusion-controlled region the reaction of acetylene was first order in hydrogen, and the rate of ethane formation was independent of both the acetylene and ethylene pressures. This latter observation is consistent with the presence of sites which can hydrogenate ethylene even in the presence of acetylene. The nature of the C_4 products has been shown to be dependent on the packing of adsorbed acetylene molecules and on the availability of surface hydrogen. The analysis of a heavy involatile product is also reported.

INTRODUCTION

Mann and Safo (*1*) have described the hydrogenation of acetylene over pumice-supported nickel, platinum, and palladium and found that the selectivity of the reaction depended on the temperature and feed ratio. In commercial practice the hydrogenation of acetylene is normally performed as a method to remove C_2H_2 from ethylene cracker streams. It has been shown (*2*) that the characteristics of the hydrogenation of mixtures of ethylene and acetylene in a static system at a pressure of 7.3 kN m^{-2} are different from those of each gas studied individually.

In that work (*2*), no evidence was found for the production of C_4 compounds, probably because of their retention on the surface of the support, but a mechanism for acetylene polymerization during hydrogenation over nickel and platinum has been reported by Sheridan (*3–5*). Analysis of the C_4 fraction produced by the reaction of acetylene over palladium (*6*) has shown that the butenes were not produced in their equilibrium proportions.

These observations prompted us to investigate the kinetics of the hydrogenation of mixtures of acetylene in ethylene in a flow system at atmospheric pressure with a view to interpreting the mechanisms of hydrogenation and polymerization. The effect of carbon monoxide, added in commercial practice to improve the selectivity of the hydrogenation, is also reported.

EXPERIMENTAL

The reactor consisted of a stainless-steel catalyst basket which could be rotated at speeds up to 6000 rpm, the speed being indicated on a tachometer. The drive unit was completely sealed from, and magneti-

0021-9517/78/0512-0173$02.00/0

cally coupled to, the reactor shaft. The details of this type of reactor have been described elsewhere (*7*). Rotation of the basket at sufficiently high speeds caused the gas phase to be perfectly mixed and the composition of the gas phase to be identical over every catalyst pellet. Under conditions employed in this work the inflowing gas was almost instantaneously mixed with the gas already in the reactor, and the exit gas composition was assumed to be identical with the bulk gas composition in the reactor. The reaction rate was thus not dependent on inlet concentrations but on the bulk reacting gas concentration.

Cylinder gases, supplied by British Oxygen Corp. or Imperial Chemical Industries, were fed via two-stage pressure regulators, Brooks flow controllers and rotameters, or capillary flow meters into a container full of glass chips which acted as a premixer. The composition of the inlet gas was determined by gas chromatography using a 2-m silica gel column at 333 K. After measurement by rotameter, the flow to the reactor was split into two, 20% of the gas being passed down the reactor shaft to prevent damage to the reactor bearings by catalyst dust. The pressure in the reactor was marginally greater than atmospheric.

The analysis of the exit flow from the reactor was performed by gas chromatography. Two sample valves allowed material to be passed to a silica gel column, for C_2 analysis, and to a 10-m propylene carbonate on Chromosorb P column at 273 K which analyzed for C_4 compounds.

Throughout this work normal conditions used were a stirrer speed of 3000 rpm, a total gas flow rate of 20 liters hr^{-1} and a temperature of 343 K. Nitrogen was used as an inert diluent so that, in experiments where the ethylene or hydrogen concentrations were varied, the total gas flow rate could be maintained at 20 liters hr^{-1}.

The catalyst used, I.C.I. type 38-3, was identical to that described previously (*2*) and was reduced for 2 hr at 473 K in a 20-liter-hr^{-1} flow of 30% hydrogen in nitrogen. The catalyst had a mean pore diameter of 8 nm and a pore volume distributed as follows: >25-nm pore radius, 0.12 $cm^3\ g^{-1}$; 3.7–25 nm, 0.07 $cm^3\ g^{-1}$; 1.0–3.7 nm, 0.16 $cm^3\ g^{-1}$. The geometric surface area of the catalyst pellets was 8 $cm^2\ g^{-1}$. All reactions were performed on the same catalyst sample; checks made at frequent intervals indicated that constant activity was maintained throughout the period of this work.

RESULTS

The reaction rates, in units of milliliters per hour per gram of catalyst, were calculated from the inlet concentration I and exit concentration E, expressed as parts per million, using the equation

$$\text{rate} = (I - E)F/10^6\, W$$

where F is the flow rate in milliliters per hour and W the catalyst weight in grams. A positive rate corresponded to a loss of reactant and a negative rate indicated the formation of a product.

The general characteristics of a typical reaction, in which the rates of appearance or disappearance of various compounds are plotted as a function of acetylene concentration, are illustrated in Fig. 1.

Disappearance of Acetylene

On increasing the acetylene concentration from zero, the rate of acetylene removal first increased and then remained constant.

The effects of change in hydrogen concentration on the rate of acetylene removal are illustrated in Fig. 2. Two points are worthy of note. First, the magnitude of the steady rate of acetylene removal increased with increasing hydrogen concentration and, for the experiments illustrated, had an order in hydrogen of 0.87 ± 0.05. Second, the acetylene concentration required to

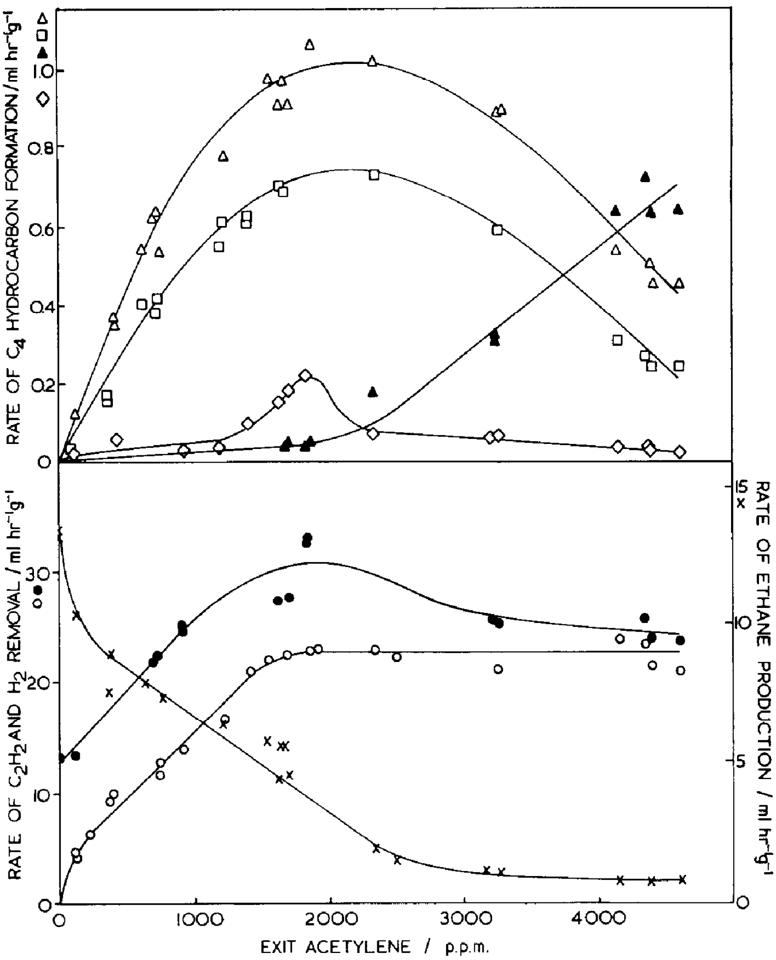


FIG. 1. Reaction at 343 K of mixtures of 25% H_2, 35% C_2H_4, 40% N_2, and 1000 ppm of CO. Rates of: ○, acetylene removal; ●, hydrogen consumption; ×, ethane formation; △, but-1-ene formation, □, *trans*-but-2-ene formation; ◇, *cis*-but-2-ene formation; and ▲, buta-1,3-diene formation at various acetylene concentrations.

achieve the point beyond which the reaction became zero order in acetylene moved to higher acetylene levels as the hydrogen level increased.

In Fig. 3 the effects of changing the concentrations of carbon monoxide and ethylene on the rate of removal of acetylene are presented. Comparison of experiments with the standard 35% ethylene in the inlet to the reactor showed that as the level of carbon monoxide was increased so the rate of acetylene removal decreased and the steady rate was established at lower concentrations of acetylene. The first 1000 ppm of carbon monoxide had a relatively greater effect than the addition of a further 4000 ppm. For experiments in the absence of carbon monoxide it was, for experimental reasons, not possible to introduce sufficient acetylene into the reactor to observe the turning point where the reaction would become zero order in acetylene.

The results of changing the inlet level of ethylene from 35% to zero, at three different concentrations of carbon monoxide, can be seen in Fig. 3. It is apparent that both the rate of hydrogenation of acetylene and the point at which the reaction became zero order in acetylene are affected by the amount of ethylene present.

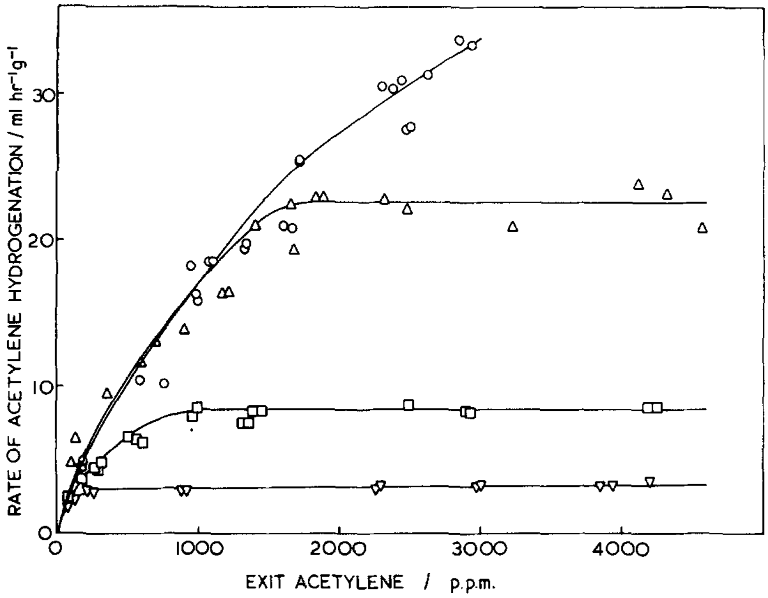


FIG. 2. Influence of hydrogen on the rate of acetylene removal at 343 K in the presence of 35% C_2H_4 and 1000 ppm of CO. Exit hydrogen: ○, 37.5%; △, 22.8%; □, 9.4%; ▽, 2.6%.

Formation of Ethane

The rates of formation of ethane at various hydrogen levels are presented as a function of acetylene concentration in Fig. 4. In the absence of acetylene the order in hydrogen was approximately unity.

Figure 5 illustrates the effect of carbon monoxide on the rate of production of

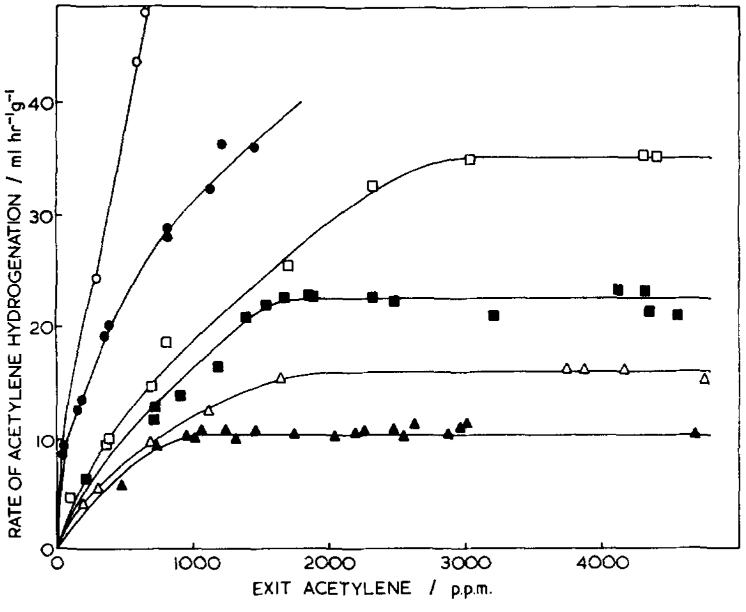


FIG. 3. Influence of ethylene and carbon monoxide on the rate of acetylene removal at 343 K in the presence of 25% H_2. Exit concentrations: ○, 0.2% C_2H_4 and 0% CO; ●, 28.7% C_2H_4 and 0% CO; □, 2.2% C_2H_4 and 1000 ppm of CO; ■, 34.4% C_2H_4 and 1000 ppm of CO; △, 1.0% C_2H_4 and 5000 ppm of CO; ▲, 34.7% ethylene and 5000 ppm of CO.

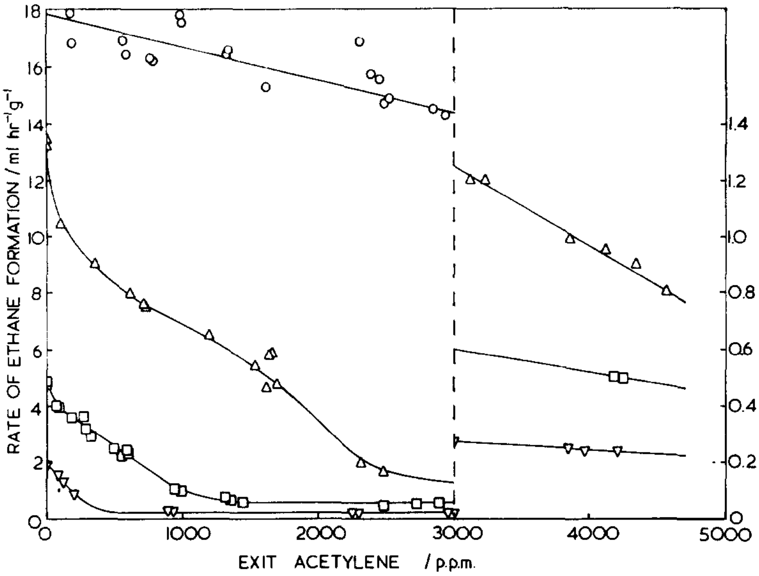


Fig. 4. Influence of hydrogen on the rate of formation of ethane at 343 K in the presence of 35% C_2H_4 and 1000 ppm of CO. Inlet hydrogen concentration: ○, 40%; △, 25%; □, 10%; ▽, 2.8%.

ethane and shows that the presence of carbon monoxide has a greater effect on the formation of ethane than on the disappearance of acetylene. It is seen that the first 1000 ppm of carbon monoxide has a disproportionately large effect on the rate of ethane formation.

Also presented in Fig. 5 is the effect of ethylene on the rate of formation of ethane for experiments conducted in the presence of 1000 ppm of carbon monoxide. With no inlet ethylene present, increasing the acetylene concentration produced an increase in the rate of ethane formation until about

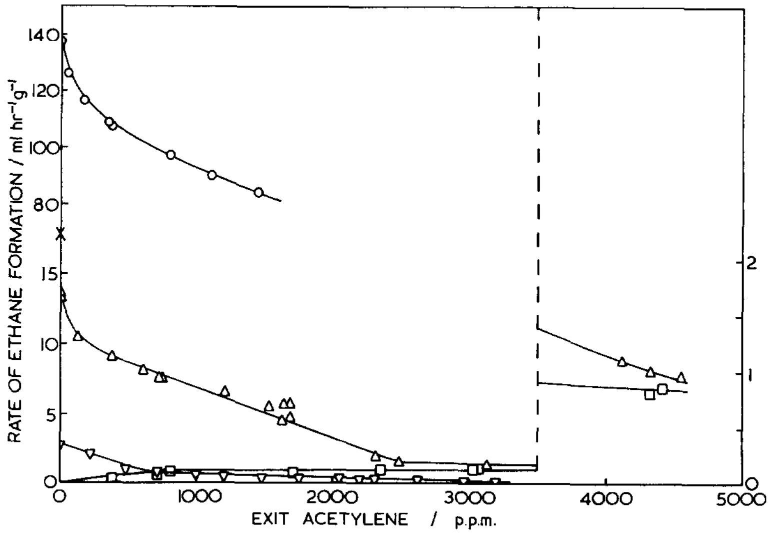


Fig. 5. Influence of ethylene and carbon monoxide on the rate of formation of ethane at 343 K in the presence of 25% hydrogen. ○, 35% C_2H_4 and zero CO inlet; △, 35% C_2H_4 and 1000 ppm of CO inlet; ▽, 35% C_2H_4 and 5000 ppm of CO inlet; □, zero C_2H_4 and 1000 ppm of CO inlet.

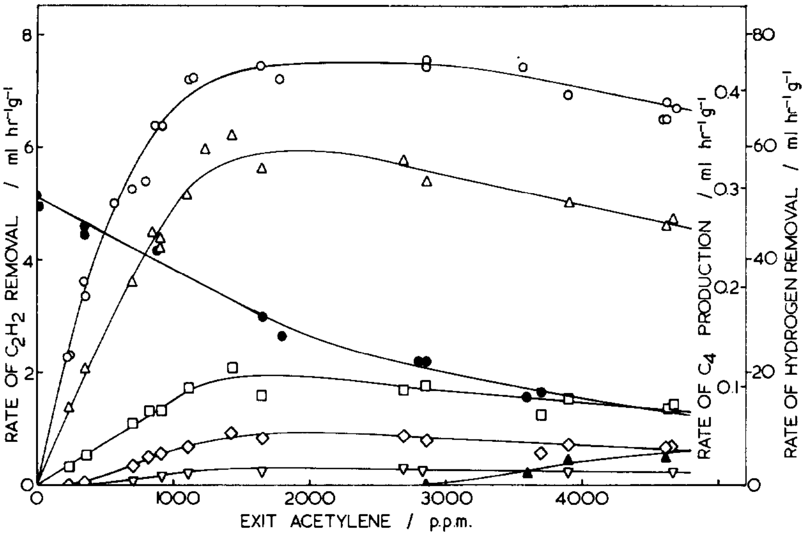


Fig. 6. Production of C_4 hydrocarbons from an experiment at 273 K with 25% H_2, 35% C_2H_4, and 40% N_2 in the absence of CO. ▽, *n*-butane; other symbols as Fig. 1.

3500 ppm of acetylene was present; further increase in the acetylene level had no effect on the rate of ethane production. It is seen that the rate of formation of ethane, at acetylene levels >3500 ppm, was identical for ethylene inlets of ~35% and zero (~2% ethylene in exit). At high acetylene concentrations the rate of ethane formation was thus independent of both the ethylene and acetylene levels and varied only with the hydrogen concentration.

Production of C_4 Hydrocarbons

Figure 6 shows the rates of hydrogenation of acetylene, hydrogen consumption, and C_4 production in a typical experiment in the absence of carbon monoxide at 273 K. As the acetylene level was increased so the rates of formation of but-1-ene, *trans*-but-2-ene, *cis*-but-2-ene, and *n*-butane also increased initially. When the acetylene concentration was increased above ~1600 ppm the rates of production of the butenes diminished and buta-1,3-diene began to appear in the gas phase. At the point where the reaction became zero order in acetylene, the C_4 composition was: but-1-ene, 66.0%; *trans*-but-2-ene, 22.1%; *cis*-but-2-ene, 9.4%; and *n*-butane, 2.5%.

The results shown in Fig. 6 for reaction in the absence of carbon monoxide may be compared with those in Fig. 1 for reaction in the presence of 1000 ppm of carbon monoxide. The temperature in the latter case was 343 K so that rates of reactions were comparable. Only traces of *n*-butane were detected in the presence of carbon monoxide. *cis*-But-2-ene was present in significant quantities only at the point where the rate of removal of acetylene had just become constant, and this point coincided with maxima in the production of but-1-ene and *trans*-but-2-ene.

The fraction of acetylene which was converted to C_4 species is plotted in Fig. 7 as a function of the acetylene concentration. It is seen that the fraction of acetylene thus converted initially increased as the acetylene in the gas phase increased until the point where the disappearance of acetylene became zero order. Figure 7 also illustrates the influence of hydrogen on the percentage of acetylene being converted into C_4 molecules. At low acetylene levels the production of C_4 species was reduced by increasing the amount of hydrogen but the converse was true at high acetylene concentrations.

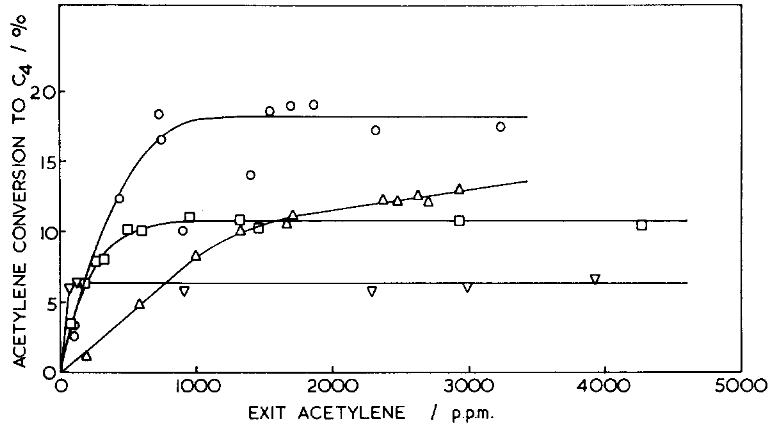


FIG. 7. Influence of hydrogen on percentage conversion of acetylene into C_4 hydrocarbons. Exit hydrogen concentration: ▽, 2.6%; □, 9.4%; ○, 22.8%; △, 37.5%.

The influence of carbon monoxide and ethylene on the fraction of acetylene forming dimer is illustrated in Fig. 8. It is seen that an increase from 1000 to 5000 ppm in the carbon monoxide concentration almost halves the yield of C_4 species. When the exit ethylene concentration was increased from ~1 to ~34.7% the fraction of acetylene dimerizing was also reduced, except at low levels of acetylene.

An experiment was carried out in an attempt to determine if the C_4 compounds were produced from two acetylene molecules, two ethylene molecules, or one acetylene molecule and one ethylene molecule. This involved carrying out reactions of acetylene in propylene and analyzing the products for C_4, C_5, and C_6 fractions. Only C_4 compounds were detected, in amounts similar to those found in experiments with ethylene, confirming that C_4 species are formed from two acetylene molecules.

After the reactor had been running for some weeks it was observed that a brown oil, probably similar in nature to the oil found in commercial acetylene removal plants, had accumulated in the exit line from the reactor. Gas chromatographic analysis of the oil showed that it consisted of at least 16 different compounds. Infrared spectra gave some evidence for the presence of some carbonyl groups and suggested that

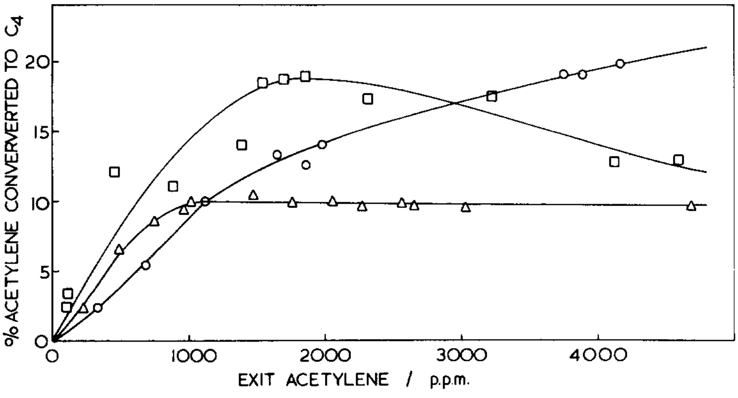


FIG. 8. Influence of ethylene and carbon monoxide on percentage of acetylene converted into C_4 hydrocarbons. □, 1000 ppm of CO, 35% C_2H_4; ○, 5000 ppm of CO, zero C_2H_4; △, 5000 ppm of CO, 35% C_2H_4.

no olefinic unsaturation was present. The ultraviolet absorption spectrum of a solution of the oil in *n*-pentane confirmed the presence of carbonyl groups. A proton magnetic resonance spectrum had two main peaks at $\delta = 0.9$ and 1.3 indicating methyl and methylene groups, respectively. Small peaks at $\delta = 2.1$ and 2.4 may be due to traces of ketonic groups. The absence of peaks at δ values between 2.5 and 10 ruled out the presence of aldehydic, aromatic, or olefinic protons. A mass spectrum of the oil produced peaks with m/e values up to 310 indicating that the longest chain present would contain 22 carbon atoms. Overall, the various analyses indicated that the oil consisted of saturated chains of up to 22 carbon atoms with traces of carbonyl groups. This analysis is consistent with that of oil found in commercial practice elsewhere (*8*).

DISCUSSION

Kinetics of the Removal of Acetylene

The shape of the plots of rate of removal of acetylene against acetylene concentration, for example in Fig. 1, may be explained on the reasonable assumption that at low acetylene levels the surface coverage in acetylene increases as the pressure of acetylene in the gas phase increases. Beyond the point when the surface becomes saturated with acetylene, no increase in rate would be expected with further increase in acetylene pressure and, indeed, none is observed.

There are two possible reasons as to why surface coverage in acetylene, at low acetylene levels, could increase with acetylene pressure. These are: (i) competition between acetylene and other species for surface sites and (ii) diffusional limitation on the rate at which acetylene can reach surface sites within catalyst pores.

Although competition between acetylene and ethylene proved to be a satisfactory explanation of the kinetics observed in static systems at lower temperatures [(*2*) and references therein], we believe that it is not the principal factor governing the surface coverage of acetylene under the conditions presently reported for the following reasons. First, the rise in rate of acetylene removal with acetylene concentration (Fig. 1) has an approximately linear portion rather than the smooth curve predicted on the basis of simple Langmuir competition.

Second, if competition between acetylene and ethylene was the most important factor governing the amount of adsorbed acetylene, then the point at which the rate became zero order in acetylene should be similar for all experiments with the same acetylene/ethylene ratio; that this is not so is evident from Fig. 2 where it is apparent that the turning point is markedly dependent on the amount of hydrogen present. Third, although competition for surface sites between acetylene and hydrogen is inevitable, if it is assumed that such competition dominates the kinetics, then it would be reasonable to expect the rate of removal of acetylene to fall at high acetylene pressures due to exclusion of hydrogen from the surface; no fall is observed.

For Knudsen flow of gases in catalyst pores the pore diameter must be smaller than the mean free path between intermolecular collisions (*9*). At atmospheric pressure the mean free path of acetylene molecules is ~50 nm (*10*). The catalyst used in the present work had a mean pore diameter of 8 nm, so Knudsen flow would be expected.

The rate of diffusion of gases is given (*11*) by

$$r_{\mathrm{D}} = \frac{\Delta c D P}{d}$$

where r_{D} is the rate of diffusion, Δc is the concentration gradient, D is the diffusion constant, P is the porosity, and d is the distance over which diffusion is taking place. During Knudsen flow the diffusion constant is reduced below the value in the free gas. We make the assumption that the diffusion constant in pores of radius >25 nm is 100%, that for 3.7- to 25-nm pores it is 50%, and for 1.0- to 3.7-nm pores it is 15% of the value in the free gas. The value for the diffusion constant of acetylene in air at atmospheric pressure is 0.1 $cm^2 s^{-1}$ and, in the absence of a literature value for ethylene/nitrogen mixtures, we have applied this in the present circumstances.

From the values quoted above and the porosity distribution cited earlier in the paper, the magnitude of the product $D \cdot P$ was calculated to be 0.018 $cm^5 g^{-1} s^{-1}$. For conditions where the concentration difference was 2000 ppm and the depth of the layer of palladium on the catalyst was 0.8 mm, the rate of diffusion of acetylene was calculated to be 2.2×10^{-8} mol $cm^{-2} s^{-1}$. For the experiment presented in Fig. 1, when the concentration of acetylene was 3000 ppm the rate of removal of acetylene was 24 ml $hr^{-1} g^{-1}$; this is equivalent to $\sim 3 \times 10^{-8}$ mol $cm^{-2} s^{-1}$ for pellets with a superficial area of 8 $cm^2 g^{-1}$. These calculations suggest that the rate of acetylene hydrogenation at low acetylene levels is controlled by the rate of diffusion within the catalyst pores. At high acetylene levels, with correspondingly high concentration gradients, diffusion is fast and the rate is controlled by the kinetics of the reaction.

It was confirmed that bulk diffusion in the gas phase was not rate limiting as the rate of reaction did not alter when the basket speed was changed within the range 2000 to 4000 rpm.

Three regions may thus be identified as the acetylene pressure increases. These will be subsequently referred to as (i) the region of diffusion control, (ii) the turning point, and (iii) the "steady" region where the rate is kinetically controlled and is approximately zero order in acetylene.

Effects of Hydrogen, Carbon Monoxide, and Ethylene on The Rate of Removal of Acetylene

It is seen from Fig. 2 that the reaction is approximately first order in hydrogen at high acetylene levels when the rate is not diffusion limited. The concentration of acetylene required to establish surface coverage and the steady rate of acetylene removal increases as the amount of hydrogen is increased, and in the experiment with 40% hydrogen, the region of diffusion control extended throughout the range of the whole experiment and no steady rate was achieved. It is interesting to note that the diffusion-controlled regions are common to all experiments in Fig. 2, such regions being intersected by horizontal lines corresponding to the different kinetic rates for each hydrogen concentration. Outside the diffusion controlled region the kinetic order in hydrogen was slightly less than unity, perhaps indicating some limited competition between acetylene and hydrogen for the surface. Further evidence for such competition is available from the pattern of C_4 products, *vide infra*.

The effects on the rates of acetylene hydrogenation of carbon monoxide and ethylene are qualitatively similar in that the region of diffusion control is curtailed and the subsequent steady rate of acetylene removal is reduced, although the magnitude of those effects is much greater in the case of carbon monoxide. In the non-diffusion-affected region the effects of added carbon monoxide and ethylene are equivalent to those from reducing the hydrogen pressure. The information presented in Fig. 3 suggests that competition between carbon monoxide or ethylene and acetylene is not important at high acetylene levels since doubling the acetylene concentration from 2000 to 4000 ppm has no detectable effect on the rate of its reaction. The reduction in both the extent of diffusion-control and the steady rates caused by the presence of carbon monoxide or ethylene may be interpreted as being due to a reduced availability of hydrogen on the surface. The influence of carbon monoxide on the adsorption of acetylene is known to be minor (*12*, *13*).

The Formation of Ethane

The general shape of the graphs for the rate of formation of ethane as a function of acetylene concentration, illustrated in Fig. 4, may be interpreted on the basis of competition between ethylene and acetylene for the surface at low acetylene pressures, although it should be remembered that such a simple picture is considerably distorted by diffusional limitation of rates. It has been shown (*2*) that such competition occurs on type X sites, on which acetylene is adsorbed with a strength 2200 times greater than that of ethylene at 293 K. The rate of formation of ethane thus, at first, falls with increase in acetylene concentration due to decreasing ethylene coverage of type X sites.

Once the surface has become effectively saturated with acetylene, the rate of production of ethane becomes independent of the acetylene and ethylene concentrations as seen from experiments (Fig. 5) conducted in the presence of 5000 ppm of carbon monoxide. The steady rate of production of ethane at high acetylene levels may be regarded as further evidence for type Y sites which can hydrogenate ethylene even in the presence of considerable quantities of acetylene (*2*). It is particularly striking to note that the rate of production of ethane in the non-diffusion-controlled region is identical for experiments with zero and 35% ethylene in the inlet to the reactor.

The effect of carbon monoxide on the rate of ethane formation is also presented in Fig. 5. The presence of carbon monoxide is seen to depress the rate of formation of ethane to a much greater extent than the rate of hydrogenation of acetylene (compare Fig. 3), implying exclusion of ethylene from the surface by carbon monoxide. A comparison of results in Fig. 5 at carbon monoxide levels of 1000 and 5000 ppm suggests that carbon monoxide can compete effectively with ethylene for both type X and type Y surface sites.

Production of C_4 Molecules

Figures 2 and 8 show that both the rate of production of and the fraction of reacted acetylene converted to C_4 species at first increase with acetylene pressure and then become constant at the point where the rate of disappearance of acetylene becomes constant. The increase in the rate of formation at low acetylene levels may be explained by the increasing surface coverage in acetylene which increases the probability of acetylene molecules occupying adjacent sites, a reasonable prerequisite for dimerization. This concept may be represented by

$$\text{rate of } C_4 \text{ production} = k\theta_{C_2H_2}{}^{n}$$

where k is a constant and $\theta_{C_2H_2}$ is the fraction of the surface covered by acetylene. An indication of the value of this fraction may be obtained from

$$\theta_{C_2H_2} = \frac{\text{rate of } C_2H_2 \text{ disappearance}}{\text{limiting rate of } C_2H_2 \text{ disappearance at surface saturation}}.$$

Values of n obtained from graphs of log rate of C_4 production against log $\theta_{C_2H_2}$ for experiments at various gas compositions are shown in Table 1. In the majority of experiments n had a value close to 2 confirming that C_4 production required the adsorption of acetylene molecules on two adjacent sites.

TABLE 1

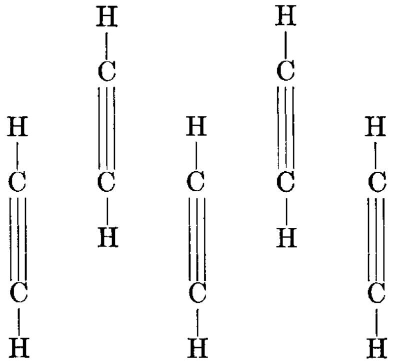
Dependence of Rate of C_4 Production on the Surface Coverage of Acetylene at 343 K

Inlet gas composition				n^a
H_2 (%)	C_2H_4 (%)	N_2 (%)	CO (ppm)	
25	35	40	1000	1.64
25	35	40	5000	2.00
25	0	75	1000	2.05
10	35	55	1000	2.00

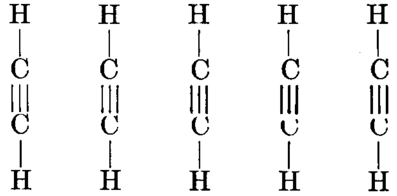
[a] As defined in text.

The composition of butenes, at the point of surface saturation with acetylene, is similar to that reported by Bond and Wells (*6*) and is markedly different from the thermodynamic equilibrium composition. This suggests that when a butene molecule is formed it is immediately desorbed, without having sufficient time to undergo isomerization; this is understandable in the presence of acetylene and large quantities of ethylene.

Sheridan has suggested (*4*) that the free radical form of an adsorbed vinyl group reacts with an adsorbed acetylene molecule to produce buta-1,3-diene which subsequently hydrogenates to butenes. On hydrogenation of buta-1,3-diene on palladium (*14*) at 273 K, the butene composition was found to agree favorably with values observed during acetylene hydrogenation (*6*) in confirmation of Sheridan's mechanism. Bond *et al.* (*14*) have proposed that but-1-ene is produced by 1,2 addition of two hydrogen atoms to buta-1,3-diene, while the but-2-enes are formed by a 1,4 addition process, the particular geometric isomer of but-2-ene being determined by the conformation of the adsorbed buta-1,3-diene. The conformation of adsorbed buta-1,3-diene resulting from the dimerization of adsorbed acetylene may well differ from that produced by gas phase buta-1,3-diene. It has been reported (*15*) that the most favored steric arrangement for acetylene molecules on palladium is a form of staggered packing,



which would be expected to form the transoid buta-1,3-diene on dimerization and subsequently the *trans*-but-2-ene on hydrogenation. At low acetylene levels the majority of the but-2-ene formed has the trans configuration (see Fig. 1). As the surface concentration of acetylene approaches monolayer saturation, the mode of packing of acetylene may change to a closer packed form with the following geometry:



This form of packing would be expected to ultimately yield *cis*-but-2-ene. Figure 1 shows that the amount of *cis*-but-2-ene formed does increase considerably when the acetylene coverage is close to saturation.

At high acetylene concentrations the yield of C_4 olefins falls and the principal C_4 product becomes buta-1,3-diene. This suggests that either the availability of surface hydrogen becomes less, although this is not reflected in a change in the rate of acetylene hydrogenation, or that the increasing intensity of acetylene bombardment of the surface with acetylene pressure displaces the buta-1,3-diene molecules before they have time to hydrogenate.

Comparison of Figs. 1 and 6 shows that the presence of carbon monoxide has the effect of decreasing the degree of saturation of the C_4 molecules produced at a given acetylene concentration, presumably by reducing by competition the availability of adsorbed hydrogen.

Recently published results (*16*) have suggested that the presence of palladium hydride phases may influence the hydrogenation of acetylene. The thermodynamics of the palladium/hydrogen system (*17*) suggest that hydride formation is, in principle, possible under the conditions used in this work. It is, however, reported (*16*) that hydride formation does not occur to any significant extent on catalysts where the palladium loading is less than 1%, and we are of the opinion that hydride formation is of no importance in this work.

ACKNOWLEDGMENTS

The authors acknowledge with thanks support from the Science Research Council and from Agricultural Division, Imperial Chemical Industries, Ltd. We are also indebted to B. M. Collins and D. Lobley for much helpful advice and discussion.

REFERENCES

1. Mann, R. S., and Safo, S. Y., *Chem. Eng. Progr. Symp. Ser.* **65**, 71 (1969).

2. McGown, W. T., Kemball, C., Whan, D. A., and Scurrell, M. S., *J. Chem. Soc. Faraday Trans. I* **73**, 632 (1977).

3. Sheridan, J., *J. Chem. Soc.*, 373 (1944).

4. Sheridan, J., *J. Chem. Soc.*, 133 (1945).

5. Sheridan, J., *J. Chem. Soc.*, 305 (1945).

6. Bond, G. C., and Wells, P. B., *J. Catal.* **5**, 65 (1966).

7. Brisk, M. L., Day, R. L., Jones, M., and Warren, J. B., *Trans. Inst. Chem. Eng.* **46**, T3 (1968).

8. Dowden, D. A., private communication.

9. Wheeler, A., *Advan. Catal.* **3**, 249 (1951).

10. West, R. C., "Handbook of Chemistry and Physics," C. R. C. Press, Cleveland, Ohio, 1974.

11. Satterfield, C. N., and Sherwood, T. K., "Role of Diffusion in Catalysis," Addison-Wesley, Reading, England, 1963.

12. Takeuchi, A., Tanaka, K., and Miyahara, K., *Chem. Lett.*, 171 (1974).

13. Takeuchi, A., Tanaka, K., and Miyahara, K., *Chem. Lett.*, 411 (1974).

14. Bond, G. C., Webb, G., Wells, P. B., and Winterbottom, J. M., *J. Chem. Soc.*, 3218 (1965).

15. Bond, G. C., and Wells, P. B., *Actes Congr. Int. Catal.*, 1159 (1960).

16. Borodzinski, A., Dus, R., Frak, R., Jaulso, A., and Palczewska, W., *in* "Proceedings Sixth International Congress on Catalysis," London, 1976.

17. Wicke, E., and Nernst, G., *Ber. Bunsenges. Phys. Chem.* **68**, 224 (1964).