STUDIES IN HETEROGENEOUS CATALYSIS PART 3.—THE HYDROGENATION OF MIXTURES OF HYDROCARBONS

BY G. C. BOND * AND J. SHERIDAN

Department of Chemistry, The University, Birmingham, 15

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Added propene has no appreciable effect on the hydrogenation of methylacetylene or allene over nickel, palladium or platinum catalysts. Mixtures of pairs of the hydrocarbons, acetylene, methylacetylene and allene, are simultaneously hydrogenated, which indicates that these substances are adsorbed with comparable strengths. These facts, and the weaker adsorption of propene and ethylene, are in accord with expectations based on associative chemisorption of unsaturated hydrocarbons.

The courses followed by the hydrogenation of methylacetylene and of allene 1, 2 indicate that these hydrocarbons are both more strongly adsorbed than propene on metals such as nickel and platinum. Their hydrogenation in the presence of added propene was therefore expected to be virtually unaffected, the hydrogenation of propene to propane, usually an otherwise faster reaction, being prevented by the exclusion of propene from the surface. We have carried out experiments which prove that propene in fact acts merely as a diluent in these reactions.

It is also of interest to know if the hydrogenation of mixtures of the very strongly adsorbed hydrocarbons acetylene, methylacetylene and allene is in any way selective towards particular species. Although some analytical difficulties are met, we have obtained strong indications that these three substances are about equally strongly adsorbed on nickel and platinum.

EXPERIMENTAL

Propene, made by the method of Davis,³ was distilled through a Podbielniak still, the middle fraction (b.p. -47.5° C) being placed in a cylinder. Samples were frozen and outgassed before use. Cylinder acetylene was purified by the method of Kistiakowsky *et al.*⁴ and dried with calcium chloride. Frozen samples were outgassed before use, and the last fractions rejected. Other materials and apparatus have been previously described.^{1, 2} In gas analysis, propene (with traces of higher olefins) was absorbed separately from ethylene in 87 % sulphuric acid, the ethylene being taken up in oleum. It was not possible to absorb allene separately from propene, or acetylene separately from methylacetylene.

RESULTS

ADDITION OF PROPENE TO METHYLACETYLENE AND TO ALLENE DURING THEIR HYDRO-GENATION.—Data for experiments of this type are summarized in tables 1 and 2. In no case had the addition of propene any marked effect on the rate of change of pressure; for example, in the reaction with methylacetylene over nickel, a pressure fall of 100 mm occurred in 29 min with added propene, and in 30 min without added propene. It is seen from the table that the amounts of propene and propane formed during reaction, those of methylacetylene (or allene) removed and of hydrogen removed, and also the yield of C_3 -hydrocarbons (as percentage of the methylacetylene or allene reacting) are all virtually unaffected by whether propene is added or not. A slight and understandable increase in propane production when propene is added appears likely.

* Present address: Department of Chemistry, Princeton University, Princeton, N.J., U.S.A.

G. C. BOND AND J. SHERIDAN

Since, in the absence of methylacetylene or allene, propene hydrogenation, with these pressures and catalysts, is usually faster than any of these reactions, there can be no doubt that methylacetylene and allene are more strongly adsorbed than propene and displace it from the surface. The deactivation of palladium towards propene hydrogenation, however, makes this conclusion less certain for that metal.

 TABLE 1.—ADDITION OF PROPENE TO METHYLACETYLENE HYDROGENATION

 (All initial pressures 200 mm of each gas; products analyzed after pressure falls of 100 mm for Ni and Pt, and of 153 mm for Pd)

catalyst	temp. °C	C3H6 added (mm)	product (mm)				C3-yield
			C ₃ H ₆ formed	C ₃ H ₈	C ₃ H ₄	H ₂	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
Ni	91	201	80	5	102	111	86
Ni	91		75	4	107	113	86
Pd	75	200	136	4	46	57	90
Pd	75		134	2	55	57	94
Pt	92	200	77	11	108	99	94
Pt	92		77	10	109	100	95

TABLE 2.—ADDITION OF PROPENE TO ALLENE HYDROGENATION

(Initial pressures 200 mm of each gas; products analyzed after pressure falls of 90 mm (Ni), 151 mm (Pd) and 102 mm (Pt))

catalyst	temp, °C	C₃H6 added (mm)	product (mm)				C2-vield
			C ₃ H ₆ formed	C ₃ H ₈	C ₃ H ₄	H ₂	~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~
Ni	77	197	73	4	117	117	90
Ni	77		75	2	111	116	89
Pd	80	200	118	8	62	59	91
Pd	80		123	4	59	58	90
Pt	47	205	59	15	117	105	87
Pt	47		73	11	108	104	92

ACETYLENE + METHYLACETYLENE.—Here the original hydrocarbons cannot be separately determined by gas analysis, but since ethylene and propene are both formed when the mixture is hydrogenated, it is clear that both acetylenes are being reduced. The course of reaction in a 1/1/1 acetylene + methylacetylene + hydrogen mixture, obtained in the manner previously described,¹ is shown in fig. 1 for a nickel catalyst at 91° C.

The courses of separate hydrogenation of methylacetylene ¹ and of acetylene were also determined with the same catalyst and temperature. The course with acetylene was similar to that found earlier ⁵ but gave a slightly higher yield of C₂-hydrocarbons (49-55 %). It was then found that the course in fig. 1 is in fairly close agreement with that predicted for the two hydrogenations proceeding independently in appropriate ratios, these being chosen to fit the observed propene and ethylene productions. For example, at a pressure fall of 163 mm, the propene and ethylene pressures found would correspond, in the separate courses of reaction, to removal of 70 mm C_2H_2 , of 52 mm C_3H_4 and a total H₂ removal of 118 mm; the saturated hydrocarbons formed should total 12 mm, and relatively involatile polymers should account for removal of (total) 30 mm of H_2 and 45 mm of acetylenes. In fig. 1 the removals of C₂H₂ and C₃H₄ total 126 mm and that of H₂ 130 mm; 13 mm of saturated hydrocarbons are found, while polymers account for 36 mm of H_2 and 45 mm of acetylenes. The agreement is seen to be fairly good. Although it is doubtful if the two hydrogenations, particularly their accompanying polymerizations, are entirely independent of each other, they appear independent as far as our analyses can show, and agreement is close enough for some reliance to be placed on the relative rates of removal of C_2H_2 and C_3H_4 which are computed from the ethylene and propene pressures. As is seen from the figures quoted, the acetylene is removed somewhat more rapidly than the methylacetylene.

In the mixture, acetylene removal occurs at about half the rate observed with the same catalyst, temperature and hydrogen pressure in the absence of methylacetylene. Methylacetylene removal in the mixture is only about a third as fast as its removal with the same catalyst, temperature and hydrogen pressure in the absence of acetylene. Thus each hydrocarbon inhibits to some extent the hydrogenation of the other; this is to a slightly greater degree than expected from increased surface coverage by hydrocarbons in the mixture, since both hydrogenations are of zero order with respect to hydrocarbons.

In the separate reactions, methylacetylene is removed faster than acetylene, but in the mixture acetylene is removed slightly faster. We therefore conclude that acetylene is preferentially adsorbed to a small extent, relative to methylacetylene, at least on parts of the surface. If, to summarize the data, we assume the unlikely condition of a uniform surface for which reactants compete, and that any mutual inhibition (other than that due to changes in surface covered by C_2H_2 or C_3H_4) affects both reactions equally, then



FIG. 1.—Course of reaction in 1/1/1 mixture FIG. 2.—Course of reaction in 1/1/1 mixture of of acetylene, methylacetylene and hydrogen acetylene, allene and hydrogen over nickel at over nickel at 91° C.

76° C.

at equal partial pressures acetylene appears to occupy about 1.5 times as much surface as methylacetylene.

When the initial acetylene pressure was dropped to 100 mm and other factors kept fixed, the course found was similar in all respects, except that acetylene removal was now only about 3/4 of the methylacetylene removal. With the above assumptions, this would mean that acetylene and methylacetylene occupy roughly equal fractions of the surface when the acetylene pressure is half that of the methylacetylene.

With 1/1/1 mixtures over platinum at 140° C a course very similar to that in fig. 1 was followed, and approximates to the sum of two reactions, the removal of acetylene by one being about 1.5 times as fast as the removal of methylacetylene by the other. The separate courses of these reactions were determined with the same catalyst, temperature and hydrogen pressure. In these binary mixtures, methylacetylene is removed about twice as fast as acetylene, and thus acetylene again suppresses to some extent the hydrogenation of methylacetylene in the ternary mixture. With the assumptions as before, acetylene would occupy about 3 times as much surface as methylacetylene when their partial pressures are equal.

G. C. BOND AND J. SHERIDAN

ACETYLENE + ALLENE.—Reaction in a 1/1/1 mixture of allene, acetylene and hydrogen was studied over nickel at 76° C. Allene and propene could not be analyzed separately,² and slight solubility of allene in the acetylene absorbant led to slightly greater uncertainties than normal in the acetylene contents, since only a rough correction could be applied. It was clear, however, that hydrogen was being removed considerably faster than acetylene. Since, in the acetylene + hydrogen reaction alone at these conditions, hydrogen is removed slightly more slowly than acetylene, there can be little doubt that allene was being simultaneously hydrogenated to an appreciable extent in the 1/1/1 mixture. If allene hydrogenation accounts for removal of any hydrogen in excess of that required for the observed extent of acetylene hydrogenation, allene and propene pressures can be estimated, the reaction course plotted as in fig. 2. (Accurate estimates of propane and ethane separately were not practicable in view of the small proportions of these gases, but the assumption that ethane and propane have equal pressures was made in these computations. Deviations from equality would not greatly influence the other pressures



FIG. 3.—Course of reaction in 1/1/1 mixture of methylacetylene, allene and hydrogen over nickel at 90° C.

found.) The data can thus be satisfactorily fitted to a course made up of two independent hydrogenations, acetylene being removed somewhat faster than allene.

With the same catalyst, temperature and pressure of hydrogen, allene alone is hydrogenated at about 4 times the rate found in the 1/1/1 mixture, and acetylene alone is hydrogenated at nearly the same rate as in admixture with allene. Acetylene, therefore, suppresses to some extent, but not entirely, the hydrogenation of allene. With the assumptions made previously, acetylene would occupy 4-5 times as much surface as allene when the partial pressures of the two gases are equal. With a similar 1/1/1mixture over platinum at 137° C the results obtained are very similar to those with nickel.

METHYLACETYLENE + ALLENE.—Though the same limiting factors in analysis were met here, it was clear that hydrogen was removed nearly twice as fast as methylacetylene from a 1/1/1 mixture of these gases and hydrogen over nickel at 90° C. Since, in methylacetylene hydrogenation alone under these conditions ¹ hydrogen and methylacetylene are removed at nearly equal rates, there can be no doubt that allene is being hydrogenated at almost the same rate as methylacetylene in the 1/1/1 mixture. By attributing the extra hydrogen removal to this reaction we are able to compute allene and propene pressures and obtain the course of reaction shown in fig. 3. Thus the data again agree with the occurrence of two simultaneous and relatively independent hydrogenations, as far as products are concerned.

With the same catalyst, temperature and hydrogen pressure, allene alone is hydrogenated about 3 times as fast as in the 1/1/1 mixture, while acetylene alone is hydrogenated only slightly faster than in the 1/1/1 mixture. Therefore methylacetylene is to some degree selectively hydrogenated in this mixture, and with the assumptions made previously it would occupy 3-4 times as much surface as allene when the two gases have equal partial pressures.

DISCUSSION

The results leave little doubt that acetylene, methylacetylene and allene are much more strongly adsorbed on the metals studied than propene is. Furthermore, the adsorptions of acetylene, methylacetylene and allene must, for much of the surface at least, be of closely similar strengths, since none can entirely prevent the others from being simultaneously hydrogenated. It appears probable that a slight decrease in strength of adsorption occurs in the order acetylene, methylacetylene and allene.

Since, in their binary mixtures, these hydrocarbons each apparently occupy comparable fractions of the chemisorbed layer, it may be deduced from the relationship given by Eley ⁶ that their heats of adsorption under the conditions studied do not differ appreciably, probably not by more than about 1 kcal/mole.

It is worth noting that this similarity in heats of adsorption is what would be expected if these hydrocarbons were chemisorbed in two-point contact, from the application of reasonable values for the heats of formation of the bonds involved, allowance being made for small differences in C—H bond strength as the C involved becomes singly, doubly or triply bonded to another C-atom. From such heats of linkage, it is also expected that associative adsorption of ethylene and propene would be about 10 kcal less exothermic than acetylene, methylacetylene or allene adsorption. The observed heats of adsorption, on sparsely covered nickel, of ethylene (58 kcal 7) and acetylene (67 kcal 8) do show this difference. Though we may not apply values for sparsely covered surfaces directly to our data, the theory of associative adsorption would lead qualitatively to the view that ethylene or propene should be almost completely excluded from the catalyst by acetylene, methylacetylene or allene, while the last three substances would be simultaneously adsorbed. The present results therefore support the theory of associative adsorption.

¹ Bond and Sheridan, Trans. Faraday Soc. (part 1).

² Bond and Sheridan, Trans. Faraday Soc. (part 2).

³ Davis, J. Amer. Chem. Soc., 1928, 50, 2778.

⁴ Kistiakowsky, Ruhoff, Smith and Vaughan, J. Amer. Chem. Soc., 1936, 58, 146.

⁵ Sheridan, J. Chem. Soc., 1944, 373; 1945, 301.

⁶ Eley, Quart. Rev., 1949, 3, 214.

7 Beeck, Physic. Rev., 1945, 17, 61.

⁸ Private communication from J. N. Wilson, Shell Development Co.