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The Hydrogenation and Oligomerisation of Propyne over an Ion-Exchanged Copper on Silica Catalyst

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The hydrogenation of propyne over an ion-exchanged copper on silica catalyst has been investigated. The system has a high selectivity for the production of propene over propane but is accompanied by the formation of oligomeric material that causes catalyst deactivation. Oligomer deposition can be readily followed by *in situ* infrared spectroscopic measurements. The amount of oligomer falls with increase in temperature and hydrogen pressure. The mechanism has been investigated through analysis of the oligomer fraction and by the use of deuterium in place of hydrogen. Greater than 70% of the C_6 products are dienes, principally *trans*-2-methylpenta-1,3-diene, *trans*-2-*trans*-4-hexadiene, and 2,3-dimethylbuta-1,3-diene. Three C_6H_8 compounds, 2-methylpent-1-ene-3-yne and the *cis* and *trans* isomers of hex-2-ene-4-yne make up the bulk of the remainder. Their amounts decrease steeply with increase in hydrogen pressure. The reaction with deuterium leads to dienes with an average of two deuteriums and ene-ynes averaging almost one deuterium. Unreacted propyne is exchanged to a significant extent very largely at the C_1 position. Product propenes contain zero to three deuterium atoms distributed throughout the vinyl part of the molecule. There is a moderate kinetic isotope effect on going from hydrogen to deuterium which affects propene production to a much greater extent than oligomer formation. The significance of these findings in relation to the steps by which hydrogenation and oligomerisation occur is discussed. © 1994 Academic Press, Inc.

INTRODUCTION

Light olefins are usually produced on an industrial scale by the steam reforming of ethane or higher hydrocarbons (1). The process also produces alkynes which must be removed to avoid interference with downstream use such as polymerisation (2). Catalytic hydrogenation is the most commonly used removal method (3). The aim is to selectively convert the alkynes to their corresponding alkenes with minimal loss through overhydrogenation to the alkane or through oligomerisation. Palladium-based catalysts (3), often moderated in some way (4, 5), offer a good compromise, but systems using copper (6, 7) or other metals have also been described. Formation of oligomers (commonly known as "green oil") occurs to some extent with all systems, particularly when compounds with multiple unsaturation (e.g., but-1-ene-3-yne) are present. Oligomers lead to catalyst deactivation through fouling.

Oligomer formation is generally explained in terms of a mechanism attributed to early work by Sheridan (8) and described in some detail by Bond (9) and others. It supposes that addition of a single hydrogen to an adsorbed alkyne produces a half-hydrogenated state which exists in two forms. One is vinyl-like with an intact double bond and the other is radical-like with single bonds only. Hydrogen addition to either state gives olefins, while addition of the radical to an adsorbed alkyne gives a dimer radical. Oligomerisation can continue until the radical converts to its vinyl counterpart and is hydrogenated. The model predicts that conjugated dienes, trienes, etc. can be formed in addition to alkenes and alkanes, and there is evidence that such compounds do make up at least part of the oligomeric fraction during the reaction of ethyne over group VIII noble metals (10). However, there is little detailed structural information, particularly for asymmetrical alkynes in which both the supposed vinyl and radical states may be bound by one of two different carbon atoms.

One of the aims of the present work was to provide such information for the hydrogenation of propyne over an ion-exchanged copper on silica catalyst. Recent work by Wehrli *et al.* (11) has shown that, under optimum conditions, such catalysts have very high selectivity for propene formation with little oligomerisation. As part of the work we have also investigated the corresponding reaction with deuterium to shed light on the rapidity of hydrogen atom transfers in the system. No previous work of this type with propyne has been reported for copper catalysts, but an extensive study by Hirota *et al.* (12) for reaction over nickel is available for comparison.

EXPERIMENTAL

Catalyst testing was carried out using a single pass flow system. The reactor consisted of an 8-mm OD by 5-mm ID pyrex tube mounted vertically in a close fitting aluminum

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block at the centre of a tube furnace controlled to ±1°C. The input feed was made up from three streams comprising a mixture of 5% propyne in helium, helium and hydrogen streams each supplied through a needle valve and ball flowmeter. A four-way valve in the hydrogen line allowed rapid interchange with a separate deuterium stream. The exit stream from the reactor flowed through three traps in series, the first connected directly to the lower end of the reactor. With the first trap at 0°C, the second at −78°C, and the third at −196°C it was possible to collect fairly pure C_9+, C_6, and C_3 fractions, respectively. Most experiments were carried out with the third trap disconnected. The exit stream (largely free of C_5+ material) was then passed to a gas sampling valve in a Shimadzu GC-8A chromatograph. It was periodically analysed using a 4-m VZN-1 column at 50°C which gave complete separation of all linear C_3 and C_4 alkanes, alkenes, and alkynes. An approximate analysis for H_2 (or D_2) was also possible.

Two batches of ion-exchanged copper on silica catalysts were made according to the procedure of Kohler *et al.* (13) and calcined at 500°C in air. Analysis by atomic absorption showed that each contained 6.0 ± 0.3% copper. Testing was carried out on 50- or 400-mg samples, crushed and sieved to a 300 to 600 μm fraction, and held at the centre of the pyrex reactor by glass wool plugs. Reduction was carried out in a flow of 1 : 1 hydrogen/helium at 50 cm^3/min in stages to 250°C over a total period of 16 h. The feed stream in most tests consisted of 2% propyne, 4–25% hydrogen, balance helium with a reactor pressure of 1 atmosphere and total flow rate of 92 cm^3 (STP)/min. Samples of the liquid fractions from the traps were diluted with dichloromethane and analysed by capillary gas chromatography using a Hewlett–Packard 5790 chromatograph and by combined gas chromatography–mass spectrometry (gc–ms) using a Kratos MS25 instrument. Each system was fitted with a 50-m BP-1 column which separates largely by boiling point. The deuterium distribution in the components of the C_6 fraction from experiments carried out with D_2 as the reductant was determined using gc–ms with correction for fragmentation on the basis of that determined when the same reaction was carried out with H_2. Corresponding C_3 fractions were analysed for deuterium without separation using a high-resolution Bruker Fourier transform mass spectrometer operated with low ionization voltage. The data were corrected for a residual fragmentation and a small amount of parent + H (or D) ions produced by ion–molecule reactions.

The C_3 material was further analysed by Fourier transform infrared spectrometry (FTIR) using a Mattson Cygnus 100 instrument operated with 0.5 cm^{-1} resolution with 40 scans accumulated for each spectrum. Spectra were recorded both on bulk trapped samples (at a known total pressure in a 10-cm cell) and using a 16-cm pathlength on-line cell through which the exit stream of the reactor was passed.

In situ infrared measurements of 50-mg pressed discs of the Cu/SiO_2 catalyst were made using the same FTIR instrument with a resolution of 4 cm^{-1} and 16 scans per spectrum. The cell used was of flow through design and identical to that described by Hicks *et al.* (14). Conversions and selectivities could be determined by analysis of the exit stream in the same way as for reaction in the tubular reactor, and pretreatment procedures were also the same.

The 5% propyne/ultrahigh purity helium stream was obtained from CIG (Australia) Ltd. Analyses showed that it also contained about 0.2% 1-butyne. Helium and hydrogen used for dilution and pretreatment were of ultrahigh purity grade. Authentic samples of 2,3-dimethylbuta-1,3-diene, *trans*-2-methylpenta-1,3-diene, *trans*-2-*trans*-4-hexadiene, and *cis*-2-*trans*-4-hexadiene were obtained from Aldrich (Wisconsin).

RESULTS

Initial testing aimed to determine if the Cu/SiO_2 catalyst behaved in the way described by Wehrli *et al.* (11). The dominant products of propyne hydrogenation were always propene and oligomers, some colourless and relatively low boiling, others quite viscous and flowing only slowly from the heated zone of the reactor. The term "green oil" was somewhat of a misnomer for the latter since the actual colour ranged from light yellow/green to black. The propane/propene ratio never exceeded 1 : 100 even for total conversion at 290°C. The total amount of oligomers formed could not be determined directly. The fractional conversion (X) was therefore calculated by difference

$$X = \frac{\text{mol\% propyne (in)} - \text{mol\% propyne (out)}}{\text{mol\% propyne (in)}}$$

and the selectivity to propene (S) as the percentage of propene formed relative to propyne reacted, i.e.,

$$S = \frac{\text{mol\% propene (out)} \times 100}{\text{mol\% propyne (in)} - \text{mol\% propyne (out)}}.$$

Since propane formation was negligible, the percentage of propyne which undergoes oligomerisation is given by $100 - S$. It should be noted that since calculation of both X and S involves differences they become less accurate at low conversions. The estimated error in each is about 1 part in 100 for X near 0.50 increasing to 1 in 10 when X is 0.10.

Figure 1 shows results obtained in tests using 400 mg of Cu/SiO_2. With this relatively large mass the conversion

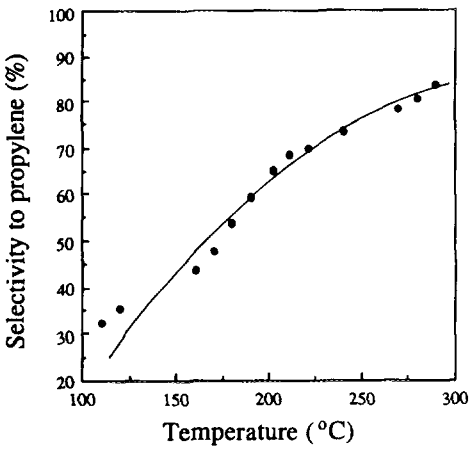


FIG. 1. Selectivity to propene as a function of temperature when hydrogenating propyne over 400 mg of Cu/SiO_2 using a feedstream of 2 mol% propyne, 8 mol% hydrogen, balance helium at 90 cm^3(STP)/min.

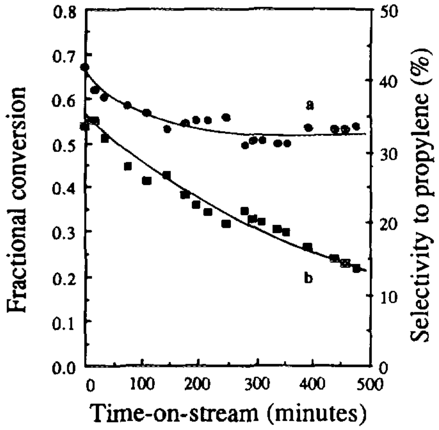


FIG. 2. Selectivity to propene (a) and fractional conversion (b) as a function of time-on-stream during reaction over 50 mg of Cu/SiO_2 at 150°C using 2 mol% propyne, 8 mol% hydrogen, balance helium at 90 cm^3(STP)/min.

was close to complete at temperatures above 140°C. Even so, as reported by Wehrli *et al.* (11), the selectivity to propene shows a characteristic rise from 30% at 100°C to 80% at 295°C. There are two possible explanations. One is that the true activation energy for hydrogenation to propene exceeds that for oligomerisation. The difference would need to be about 23 kJ/mol to explain the trend. Alternatively, the kinetics may be different. If, for example, the rate determining step in hydrogenation involved both adsorbed hydrogen and adsorbed propyne, whereas that producing oligomerisation required adjacently adsorbed propyne, then the rate ratio for the two reactions would be proportional to $\theta_H\theta_P/\theta_P^2$ or θ_H/θ_P where the θs are fractional coverages. In this case the rate ratio should increase (i.e., selectivity improve) if θ_P declines with increase in temperature faster than does θ_H. This is expected on the grounds that the heat of adsorption of propyne on copper should be greater than that of hydrogen.

While deactivation was not apparent in the results shown in Fig. 1, it was quite obvious when using catalyst masses which gave less than complete conversion. Figure 2 shows the time-on-stream behaviour when using 50 mg of Cu/SiO_2 at 150°C. Conversion declined from an initial value of 0.57 to 0.20 after 8 h. The reaction rate, calculated according to the differential reactor approximation, was then 5.5 mmol (C_3H_4)/kg/s in close agreement with a value calculated from the activation energy plot of Wehrli *et al.* (11). As shown in Fig. 2, the selectivity was little affected by catalyst deactivation. After a small decline over the initial 2 h, it was constant at 34 ± 3% under the conditions used.

The continuous deactivation made it difficult to determine kinetic orders with the system, especially as it was necessary to take the catalyst off-line when resetting partial pressures. The apparent behaviour was similar to that reported by Wehrli *et al.* (11) (i.e., close to first order in hydrogen and zero order in propyne) but with one significant difference. In experiments at temperatures of 150°C or more using substantially deactivated catalysts, selectivity always increased with hydrogen pressure. Results are shown in Fig. 3. This is consistent with the simple model described previously which predicts that the ratio of the hydrogenation rate to the oligomerisation rate should increase with hydrogen coverage (and hence hydrogen pressure if the hydrogen coverage is incomplete). In experiments at 100°C and 130°C Wehrli *et al.* (11) observed no dependence of selectivity on hydrogen pressure. Possibly site coverage by hydrogen is close to complete at these lower temperatures.

Samples of the oligomeric material from a number of runs were collected and analysed by capillary gas chromatography and gc–ms. Upwards of 100 compounds were observed. Identification of all peaks was impossible but the number of carbon atoms and hydrogen atoms in many

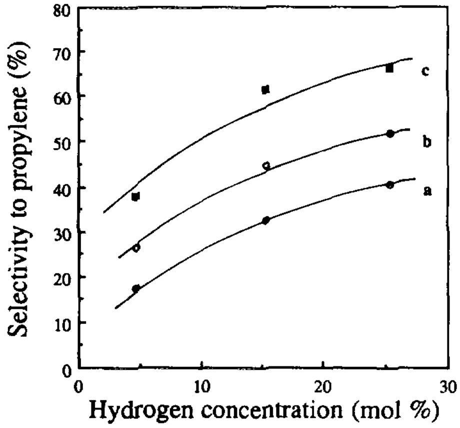


FIG. 3. Selectivity to propene as a function of hydrogen concentration during reaction over 50 mg of Cu/SiO_2 with 2% propyne, balance hydrogen plus helium to 90 cm^3(STP)/min. (a) 150°C; (b) 170°C; (c) 200°C.

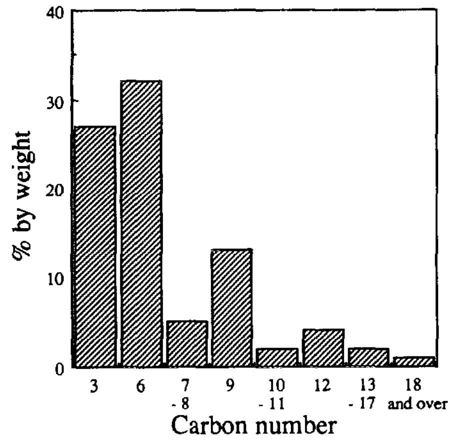


FIG. 4. Product histogram for reaction using 2% propyne, 4% hydrogen, balance helium to 93 cm^3(STP)/min over 50 mg of Cu/SiO_2 at 150°C. The product distribution is expressed as wt% of propyne lost to products other than propene.

could be worked out from the *m/z* value of the parent ions in their mass spectra. Figure 4 gives the product histogram for one experiment at 150°C using 4% hydrogen in which the conversion and selectivity to propene, averaged over the collection time of 3 h, were 0.51 and 28%, respectively. As expected, compounds with multiples of three carbon atoms predominate (The C_7 and C_{10} compounds probably arise through incorporation of the 1-butyne impurity in the feed into oligomeric material). Under these conditions the C_6 products, taken together, exceed propene in the products and there is a steady falloff in going to C_9, C_{12}, C_{15}, etc. Approximately 15% (0.3 g/g (catalyst)) is unaccounted for as still higher molecular weight material retained in the reactor, largely on the catalyst itself. The amounts retained in different experiments could not be determined with sufficient accuracy to decide if the above value represented an equilibrium one or might depend on the conditions used.

The buildup in higher molecular weight material on the catalyst could be readily seen in *in situ* infrared spectroscopy of a catalyst disc as shown in Fig. 5. These measurements were carried out with 8% propene included in the feed which has the effect of lowering conversion and increasing selectivity (11). Even so, bands due to CH_3 stretching and bending vibrations built up rapidly reaching absorbances exceeding 1.0 in just 30 min. The peak positions indicate that the material deposited was significantly hydrogenated, with only a weak band at 1640 cm^{-1} due to carbon–carbon double bonds. A preponderance of methyl rather than methylene groups was also observed. Bands due to acetylenic vibrations were not observable.

The C_6 fractions from a number of experiments were analysed under optimum conditions of separation. The gc–ms results showed that most of the compounds present gave parent ions with $m/z = 82$ (i.e., C_6H_{10}) and fragmen-

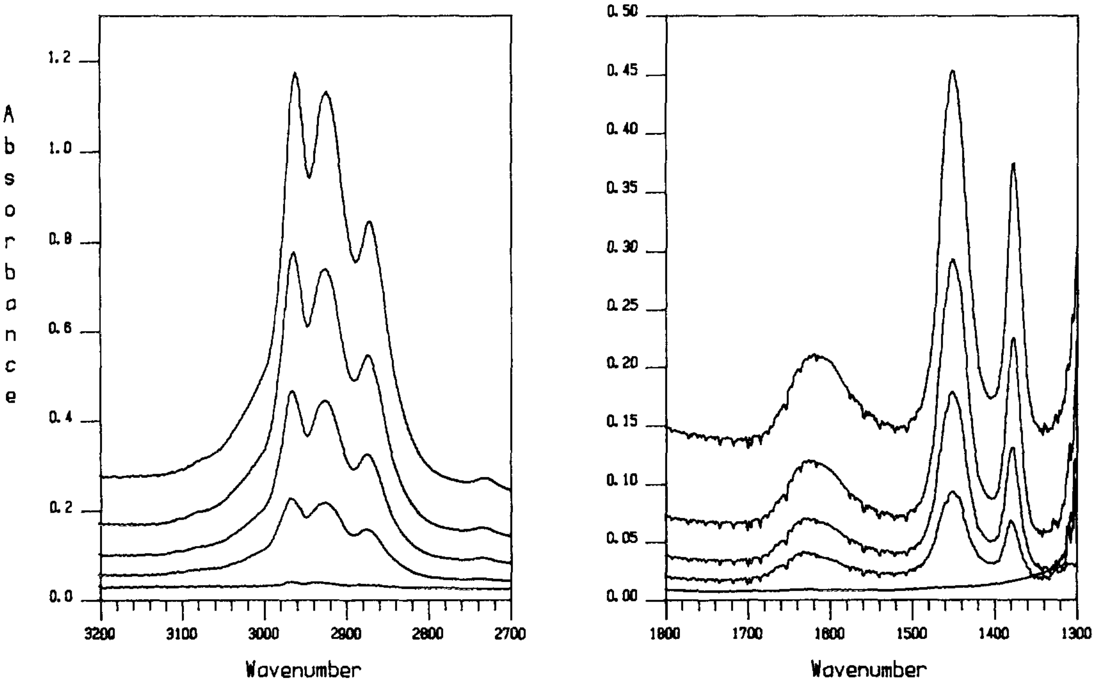


FIG. 5. *In situ* infrared spectra of 50-mg disc of Cu/SiO_2 as a function of time-on-stream during reaction of feedstream containing 2% propyne, 8% hydrogen, 8% propene, balance helium to total flow of 46 cm^3(STP)/min at 160°C. The conversion and selectivity were approximately 0.25 and 43%, respectively. The spectra were recorded in succession after reaction times of 0, 5, 15, 30, and 60 min, respectively and a background spectrum of the disc immediately following reduction has been subtracted from each.

TABLE 1

Analytical Information for C_6 Fraction from Three Experiments Using Different Hydrogen Pressures[a]

Retention time (min)[b]	Molecular formula	Identification	Hydrogen concentration 4%	8%	15%
4.59	C_6H_{10}	Unidentified	2.9	2.5	7.0
4.70	C_6H_{10}	2,3-Dimethylbuta-1,3-diene	8.1	6.0	7.0
5.26	C_6H_{10}	*trans*-2-methylpenta-1,3-diene	28.1	28.8	27.7
5.88	C_6H_{10}	Unidentified	~1	~1	~1
6.00	C_6H_{10}	*trans*-2-*trans*-4-hexadiene	15.1	19.8	20.4
6.38	C_6H_8	2-Methylpent-1-ene-3-yne	11.5	10.4	3.3
6.54	C_6H_{10}	*cis*-2-*trans*-4-hexadiene	3.5	4.0	11.4
7.01	C_6H_{10}	Unidentified	<1	~0.8	3.1
7.90	C_6H_8	*cis*-hex-2-ene-4-yne[c]	8.4	6.9	4.0
9.16	C_6H_8	*trans*-hex-2-ene-4-yne[c]	19.3	16.9	2.6

[a] All reactions at 150 to 170°C using 2% propyne in helium/hydrogen with total flow of 92 cm^3(STP)/min over 50 mg of Cu/SiO_2.

[b] Using 50-m BP-1 column at 20°C for 4 min then programmed at 2°C/min.

[c] The mass spectra of these two compounds are almost identical but the identification can be made on the basis of boiling point difference since the *cis* isomer has a significantly lower boiling point (16).

tation patterns characteristic of C_6 dienes. The four such compounds present in greatest amount could be identified by comparison of retention times and mass spectral patterns against those of authentic samples. However, three relatively large peaks exhibited parent ions with m/z = 80 (i.e., C_6H_8) and patterns which matched those for isomeric C_6 ene-ynes in a mass spectral library. Table 1 gives the results for experiments at 150°C using three different hydrogen concentrations. In each case *trans*-2-methylpenta-1,3-diene was formed in the greatest amount and, together with three other identified C_6H_{10} isomers (in order of abundance, *trans*-2-*trans*-4-hexadiene, 2,3-dimethylbuta-1,3-diene, and *cis*-2-*trans*-4-hexadiene), they made up more than 50% of the entire fraction. Three other C_6H_{10} compounds (two of which are probably *cis*-2-methylpenta-1,3-diene and *cis*-2-*cis*-4-hexadiene) amounted to a further 5–12%. The three ene-ynes composed almost 30% of the fraction in the experiments using 4% hydrogen but much less with 15% hydrogen. Cyclohexene and benzene were both below the detection limits and thus cyclisation is minimal at the dimer stage.

Experiments of two types were carried out to compare the rate of reaction using D_2 as compared to H_2. Figure 6 gives results for reactions carried out at 150 to 180°C with a fresh catalyst sample for each run. It is clear that both conversion and selectivity are lower with D_2 than

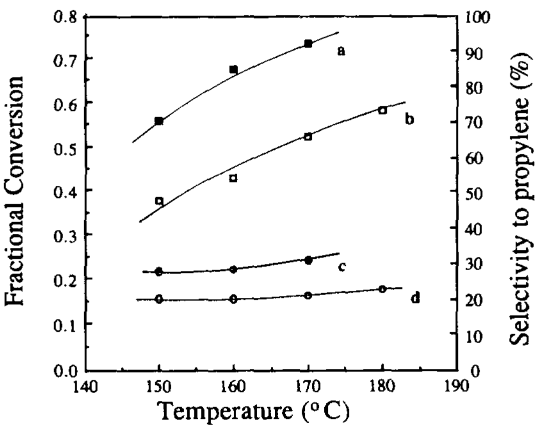


FIG. 6. Comparison of fractional conversion and selectivity to propene using D_2 versus H_2 over 50 mg Cu/SiO_2 with 2% propyne, 4% H_2 (or D_2), balance helium to 90 cm^3(STP)/min. (a) Conversion using H_2; (b) conversion using D_2; (c) selectivity using H_2; (d) selectivity using D_2.

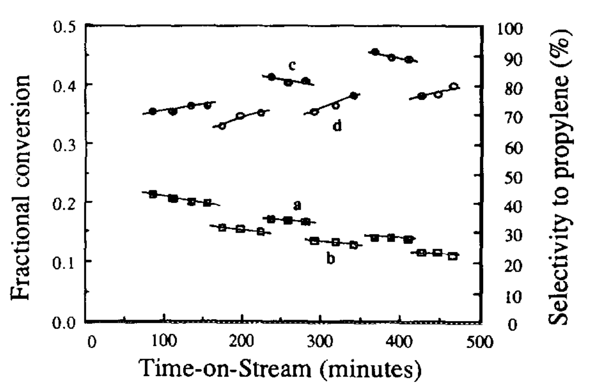


FIG. 7. Effect of alternation of H_2 and D_2 during reaction over 50 mg of deactivated Cu/SiO_2 at 260°C with 2% propyne, 4% H_2 or D_2, balance helium to 90 cm^3(STP)/min. (a) Conversion using H_2; (b) conversion using D_2; (c) selectivity to propene using H_2; (d) selectivity to propene using D_2.

TABLE 2

Mass Spectral Results for Deuterium Distributions in Major Components of C_6 Fraction

Compound analysed	C_6 fraction (%)	Deuterium distribution (%)					Mean deuterium number
		d_0	d_1	d_2	d_3	d_4	
2,3-Dimethylbuta-1,3-diene	10	6	26	38	24	7	2.0
trans-2-methylpenta-1,3-diene	40	18	29	28	19	6	1.7
trans-2-*trans*-4-hexadiene	14	13	32	33	18	3	1.6
cis-2-*trans*-4-hexadiene	3	6	27	36	25	6	2.0
2-Methylpent-1-ene-3-yne	5	53	41	5	~1	0	0.5
cis-hex-2-ene-4-yne	6	42	36	21	~1	0	0.8
trans-hex-2-ene-4-yne	19	29	44	16	~1	0	0.8

Note. For reaction of a 2 mol% propyne and 4 mol% D_2 feed stream over 52 mg of Cu/SiO_2 at 210 to 230°C giving mean conversion ≈ 0.45 and mean selectivity ≈ 33%.

with H_2 and that a kinetic isotope effect exists to some extent. The mean rate ratios, calculated separately for propene and oligomers using

$$\frac{\text{rate}\,(H_2)}{\text{rate}\,(D_2)}(\text{to propene}) = \frac{X(H_2)S(H_2)}{X(D_2)S(D_2)}$$

and

$$\frac{\text{rate}\,(H_2)}{\text{rate}\,(D_2)}(\text{to oligomers}) = \frac{X(H_2)[100 - S(H_2)]}{X(D_2)[100 - S(D_2)]}$$

were 2.0 and 1.3, respectively. The above equations are strictly true only if the reaction is zero order in propyne and hydrogen consumption is sufficiently small that the differential reactor approximation holds. A further uncertainty lies in the fact that the catalysts were deactivating over the time period to analysis and there could be no guarantee that this proceeded to the same extent with D_2 as with H_2.

Further determinations were carried out at a higher temperature (260°C), using a deactivated catalyst and alternating between H_2 and D_2. Results are shown in Fig. 7. Again conversion and selectivity are lower with D_2 than H_2. The rate ratios for the two reactions (calculated as above) are 1.4 and 1.0, respectively, which are both lower than in the previous experiment. One expects kinetic isotope effects to decline with increase in temperature but the difference is greater than expected on that basis alone, perhaps because of different deactivation rates with H_2 and D_2. Regardless of the cause the experiments are unequivocal in showing that use of D_2 in place of H_2 has a much greater effect on the rate of propene formation than on the rate of oligomer formation. The magnitude of the effect is similar to that observed by Inoue and Yasumori (15) for the conversion of ethyne to ethene on a palladium catalyst.

Mass spectral analysis of the deuterium distribution in the C_6 fraction collected after two hours from the commencement of reaction in an experiment using 4% D_2 gave the results shown in Table 2. All four dienes contain 0 to 4 deuterium atoms with mean deuterium numbers in the

TABLE 3

Mass Spectral Results for Deuterium Content of C_3 Material from Reaction of Propyne and D_2 over Cu/SiO_2

Temperature (°C)	Fractional conversion	Selectivity (%)	Species	C_3 material (%)	Deuterium distribution (%)					Mean deuterium number
					d_0	d_1	d_2	d_3	d_4	
230[a]	0.40	33	Propyne	62	91	9	<1	—	—	0.10
			Propene	38	10	30	34	21	<6	1.8
227[b]	0.95	61	Propyne	8	22	69	9	—	—	0.9
			Propene	92	3	16	36	44	≤1	2.2
197[b]	0.59	39	Propyne	64	83	17	<1	—	—	0.17
			Propene	36	13	30	41	16	—	1.6
197[b]	0.41	41	Propyne	78	94	6	—	—	—	0.06
			Propene	22	12	28	38	22	—	1.7

[a] Experimental conditions as per Table 2.

[b] This experiment was commenced at ≈227°C using 2% propyne and 8% D_2 and the temperature reduced to 197°C after 2 h. The three samples were collected over the time intervals 1–2 h, 2.5–3.8 h, and 4–5 h, respectively.

TABLE 4

Distribution of Individual Isomeric Propenes from Reaction of Propyne and D_2 over Cu/SiO_2[a]

			Isomer distribution (%)						
Temperature (°C)	Fractional conversion	Selectivity (%)	d_0	*cis*-1-d_1	*trans*-1-d_1	2-d_1	1,1-d_2	*cis* + *trans* 1,2-d_2	1,1,2-d_3
227	0.95	61	6	2	4	10	13	22	42
197	0.59	39	15	4	8	20	9	29	15
197	0.41	41	13	3	7	17	9	29	22
	Analysis method		[b]	[c]	[c]	[b]	[b]	[d]	[e]
	FTIR wavelength (cm^{-1})		576.2	800.2	974.9	549.2	728.6	[f]	[f]

[a] Conditions as per footnote b to Table 2.

[b] Direct determination by FTIR with calibration.

[c] Determined by FTIR using extinction coefficients calculated from data in Ref. (19) adjusted to resolution of instrument used.

[d] Difference between mass spectral determination of total d_2 and the FTIR determination of the 1,1-d_2 isomer.

[e] Assumes that the d_3 content determined by mass spectrometry consists of only this isomer.

[f] Observable at 877.1 cm^{-1} (*cis*-1,2-d_2) and 712.2 cm^{-1} (1,1,2-d_3) but quantitation impossible.

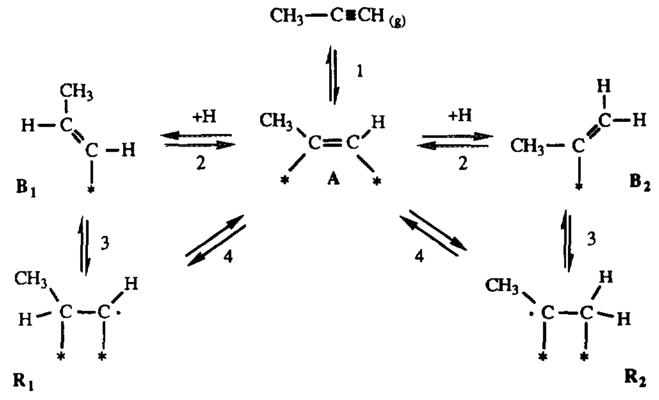
range 1.6 to 2.0. The three ene-ynes comprise mostly d_0 and d_1 material, some d_2, but with a sharp cutoff above that. The mean deuterium numbers are somewhat less than 1.0.

Table 3 shows the deuterium distribution in the C_3 fraction from the same experiment, together with that for three fractions derived from another experiment using 8% D_2 which was commenced under conditions giving a very high initial conversion. In the latter situation the propyne is largely singly deuterated with a small amount of d_2 material as well. However, the extent of deuterium incorporation is lmuch less at lower conversions. FTIR spectra showed that exchange was very largely confined to the alkyne position. Saturated CD stretching hands were almost absent while strong bands occurred at 2616 and 498 cm^{-1} due to stretching and out-of-plane bending modes of $\equiv$C–D groups (17).

It is apparent from Table 3 that there is a wide spread of deuterium in the propenes with roughly equal amounts of d_1 and d_2 but significant quantities of d_0 and d_3 as well. Small amounts of d_4 could be present but this is rather uncertain due to the need for corrections for ion–molecule reactions in the mass spectrometer. The 500–1000 cm^{-1} region of the FTIR spectra of the C_3 products contained many sharp peaks which could be assigned to the wagging and twisting vibrations of vinyl groups in deuterated propenes. There are eight such propenes with undeuterated methyl groups and six could be positively identified as present by comparison with spectra of authentic samples, or with literature spectra. Table 4 gives an approximate isomer analysis for the propenes produced in the second series of experiments of Table 3. The results for the d_0, 2-d_1 and 1,1-d_2 isomers are based on interpolation on Beer–Lambert plots for different pressures of authentic samples in the same cell and should be quite accurate. Those for the two 1-d_1 isomers are more approximate, since they rely on extinction coefficients estimated from literature spectra (18, 19) and adjusted to the higher resolution used for the present measurements. Even so it seems likely that the reaction produces more of the *trans* than the *cis* isomer. Bands due to the *cis*-1,2-d_2 isomer could be positively identified by comparison with a literature spectrum (20) but quantitation proved impossible. The spectra also showed a band at 712.2 cm^{-1} which can be assigned to the 1,1,2-d_3 isomer on the grounds that it is very close to that observed for C_3D_6 which has the same vinyl group. Several further bands remained unassigned and are presumably due to the *trans*-1,2-isomer.

DISCUSSION

According to the Sheridan scheme (8) for the hydrogenation of ethyne three types of adsorbed species are present: the associatively adsorbed ethyne and a vinyl-type half-hydrogenated state plus its radical counterpart. Starting from propyne both the latter can conceivably exist in two forms depending on the carbon to which the hydrogen is added. The adsorption scheme can thus be represented by



where * is an adsorption site. The radicals are shown in an odd electron arrangement in the spirit of Sheridan's original suggestion but they could be equally well represented as transient species with the appropriate carbon bound to two adjacent copper atoms.

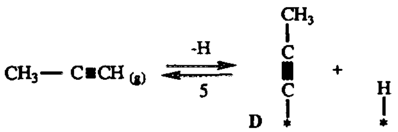
Propene can then be formed by addition of a hydrogen atom to B_1, B_2, R_1, or R_2. Oligomer formation may be initiated by addition of radical R_1 or R_2 to either carbon 1 or carbon 2 of species A. If R_1 attacks carbon 2, or R_2 attacks carbon 1, then this forms a dimer radical

$R_1 + A(C_2)$

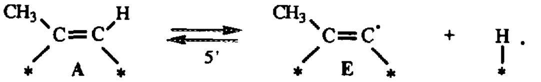
$R_2 + A(C_1)$

which may be polymerized further to give 2-methylpenta-1,3-diene after hydrogen addition and desorption. The equivalent process with R_1 adding to carbon 1 would give a hexa-2,4-diene, while R_2 adding to carbon 2 would produce 2,3-dimethylbuta-1,3-diene. Radical R_1 cannot give rise to the latter, nor can R_2 give rise to linear hexadienes. Since linear, and singly branched and doubly branched dienes are all produced, one infers that both forms of the radical must be present. By extension, if step 3 exists, then both B_1 and B_2 must be present. Since the quantity of linear hexadienes exceeds that of the dimethylbutadiene (Table 1) one infers that R_1 must be present in greater amounts than R_2. However, R_2 (a secondary radical) is more stable than R_1 (primary) and thus would be expected to form more easily from B_2 than does R_1 from B_1. It follows that B_1 must be significantly more abundant than B_2, i.e., that hydrogen addition takes place preferentially at C_2 of species A. It should be noted that the scheme requires that oligomerisation beyond C_6 must necessarily involve a branched radical at each addition for the process to continue. High polymers, such as those revealed by the *in situ* infrared measurements of Fig. 4, should therefore contain many side-chain methyl groups as is observed.

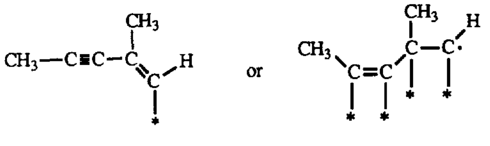
Thus the composition of the C_6 dienes and high polymers is consistent with the Sheridan scheme. However, the formation of the ene-ynes and deuterium exchange at carbon 1 of propyne implies the existence of an additional process such as



or hydrogen detachment from A



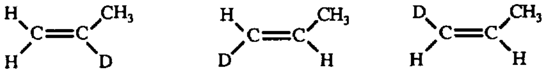
The end C–H bond in acetylenes is weak so detachment of its hydrogen would not be unexpected. Addition of either D or E to A could then give



(or the corresponding linear species if reaction were at carbon 1). Addition of a further hydrogen then gives 2-methylpent-1-ene-3-yne (or the *cis* or *trans* linear counterparts) as observed. If hydrogen pressure is increased then A should be favoured over D or E on mass action grounds and hence dienes should be produced in preference to ene-ynes again as observed.

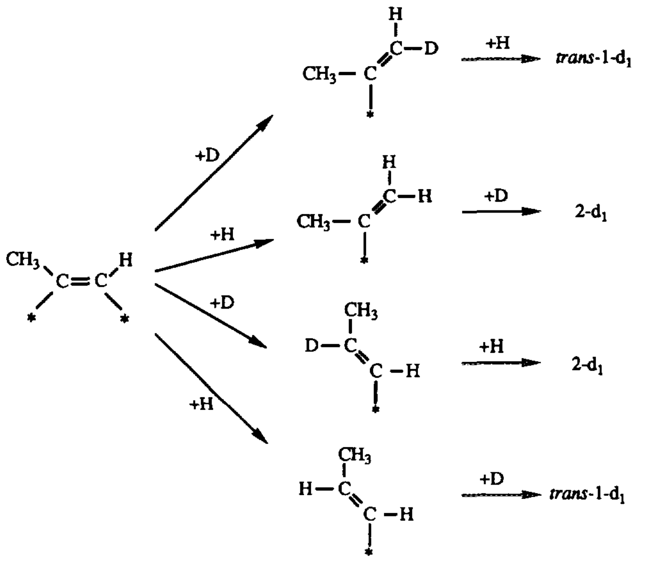
The results for the experiments using D_2 support the above picture. Reversal of step 5 (using D) produces exchanged propyne. The ene-ynes should average about one deuterium representing the one required to release the above species. The dienes should average two deuteriums since their formation requires two additions. There are two consequences of propyne exchange even though it is incomplete. Firstly, its re-adsorption provides some A with deuterium on carbon 1 and hence a route to 1,1-d_2 and 1,1,2-d_3 propenes. Secondly, it deposits hydrogen on the copper which may be used for hydrogenation of B and/or R thus giving d_1 (and even d_0) propene.

Some measure of the speed of the various steps and the species involved is provided by the relative amounts of the three d_1-propenes



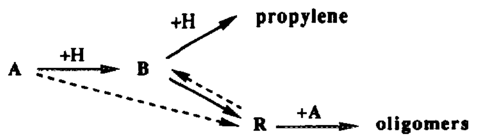
2-d_1 *trans*-1-d_1 *cis*-1-d_1

The data indicate that the amount of *cis*-1-d_1 is much less than either 2-d_1 or *trans*-1-d_1. If this is correct, and the finding is very similar to the much more accurate microwave analyses of Hirota *et al.* (12) for the corresponding reaction over nickel, the species B and R cannot be at equilibrium since this would infer a *cis* : *trans* ratio near one. It also makes the direct steps from A to R, or from R to propene, rather unlikely since such processes could not lead to the *trans* isomer being favoured over the *cis* isomer (unless the geometry of R were fixed in such a way that both additions to A necessarily took place from the same side). It therefore appears that the favoured pathways to d$_1$-propenes are



Formation of *cis*-1-d$_1$ would be unlikely in such a scheme, since it would require prior exchange of propyne followed by two hydrogen additions. The amount formed could reflect this process, or some isomerisation via a limited amount of R → B interconversion. More accurate analysis, plus that for the two 1,2-d$_2$ isomers, could help to confirm such a picture.

The above interpretation indicates that the major hydrogenation route does not involve the radicals R$_1$ and R$_2$. Rather the basic scheme is simply



with the A → R and R → B steps fairly slow if present at all. This is consistent with the increase in selectivity with hydrogen pressure (which will favour hydrogen addition to make propene) and with temperature (which will reduce the coverage by A and hence the likelihood of oligomerisation). It is also consistent with the isotope effect for H_2 versus D_2 being larger for propene formation than for oligomer formation. The origin could be either thermodynamic, since the adsorption of H_2 on metals is expected to exceed that of D_2 above room temperature (21, 22), or kinetic, on the usual grounds that a Cu–D bond will be stronger than that of a Cu–H bond because of the zero point energy effect and hence that addition of D should be slower than that of H (23).

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