Catalytic coupling of propyne on Cu{111}

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The chemistry of propyne on Cu{111} is very different from that of ethyne. Instead of trimerising, propyne undergoes coupling reactions in which two molecules react to yield either benzene, with elimination of hydrogen, or C_6 dienes. These two processes occur with approximately equal probability. A plausible mechanism for benzene formation involves *head-to-tail* interaction of two propyne molecules. 1,4-cyclohexadiene is a likely intermediate in this process, its formation being rate determining. Propyne trimerisation is sterically inhibited by the methyl group. However, the first stage in this process does seem to occur, namely formation of a dimethyl-metallopentacycle intermediate. This may be ascribed to *head-to-head* coupling of two propyne molecules. This metallocycle undergoes either hydrogenation to C_6 dienes or disproportionation to butadiene and ethyne.

Keywords: propyne, copper, coupling, intermediates, benzene, dienes

1. Introduction

Ethyne coupling reactions catalysed by Cu [1], Pd [2] and Pd/Au [3,4] single-crystal surfaces constitute an interesting class of processes which, depending on the conditions, can yield a variety of linear and cyclic products. The key process involves dimerisation to form a C_4H_4 metallocycle. This intermediate can then react further: benzene formation, the prototype reaction, involves addition of a third ethyne molecule. Experimental and theoretical studies dealing with many structural, kinetic and mechanistic aspects of ethyne trimerisation have appeared (see [1] and references therein) and the topic has also been reviewed [5]. The bonding of the reactant, intermediate and product are well established and the mechanism of this structure sensitive reaction is understood in considerable detail.

Ethyne trimerisation is generally an efficient process. Thus on Pd(111) $\sim$60% of a saturated overlayer undergoes conversion to benzene in a single TPR sweep; (111)-oriented Pd/Au surfaces are $\sim$80% efficient in this sense. Over Cu(110) [1] and Cu{111} [6] the reaction proceeds at low temperatures with close to 100% efficiency. Although the overall reaction mechanism is the same on both Cu- and Pd-based surfaces, there are important kinetic differences. On the Cu surfaces benzene evolution into the gas phase is a surface reaction rate limited process, whereas on the Pd-based surfaces it is desorption rate limited.

The analogous coupling reactions of propyne are of interest because they introduce additional interesting stereochemical factors. By analogy with ethyne, one might expect propyne trimerisation to lead to a mixture of 1,2,3-, 1,3,4- and 1,3,5-trimethylbenzenes. Such reactions are indeed observed [7] on $TiO_2\{001\}$. Given the similarities between the structure, bonding [8,9] and reactivity of ethyne on Pd(111) and Cu{111} surfaces, it might be expected that propyne trimerisation on Cu{111} would also be an efficient process. Here we show that propyne does *not* trimerise on Cu{111} – instead, two molecules couple yielding either benzene with elimination of hydrogen, or a product detected at 82 amu, accompanied by production of propene and a small amount of butadiene. In addition, the overall catalytic activity is substantially lower than that observed for ethyne. Plausible reaction intermediates for the formation of benzene and the 82 amu product are investigated and an overall reaction scheme is deduced.

2. Experimental

Experiments were performed in a UHV/XPS/LEED apparatus, described previously [10], which operated at a base pressure of 1×10^{-10} Torr. The Cu{111} sample could be resistively heated to 850 K and cooled to 110 K. Cleaning was achieved by cycles of Ar^+ sputtering (6×10^{-2} A m^{-2}, 500 eV, 810 K) and annealing to 810 K in vacuum. XP spectra were obtained with Al K_α radiation (1486.7 eV) using a VSW HA100 single-channel analyser. All gas dosing was performed at 120 K, unless otherwise stated, using a tube doser to enhance the flux at the sample position. Propyne was obtained from CK Gases (99.33%) and purified by passage though a trap maintained at 180 K before entering the UHV chamber. 1,2,4-trimethylbenzene (TMB), cyclohexene, 1,3-cyclohexadiene and 1,4-cyclohexadiene were obtained from Fluka Chemicals and purified by freeze–pump–thaw cycles. Their purities were verified by mass spectrometry. Quoted exposures are in langmuirs ($1\ \mathrm{L} = 10^{-6}$ Torr s) and are uncor-

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rected for ion gauge sensitivity. For TPD/TPR measurements (∼4 $\mathrm{K\,s^{-1}}$) the sample was positioned ∼2 cm from the quadrupole mass spectrometer (QMS) ioniser so that the signal arose almost entirely from the front face. Integrated product yields derived from the TPD/TPR data have been corrected to allow for mass discrimination effects in the QMS, ionisation cross-sections, and the cracking patterns of relevant desorbing species. The quoted errors in product yields include those arising from this data analysis procedure.

3. Results and discussion

At 120 K propyne adsorbs to saturation coverage on Cu{111} yielding an ordered overlayer whose LEED pattern corresponds to three equivalent domains of a $(\sqrt{3} \times 4)$ R30° structure and a coverage of 0.25 monolayers (ML). That is, 0.25 propyne molecules per surface Cu atom – this figure being used to provide a calibration for the XPS intensity data. Figure 1 shows TPR spectra obtained after dosing 0.5 L propyne on Cu{111} at 120 K; they correspond to an initial propyne coverage of 0.02 ML. The data have been corrected for fragmentation pattern interferences and mass spectrometer sensitivity, as described above. It is apparent that, compared to ethyne, the overall chemical activity is relatively low – the major desorbing species at 265 K is unreacted propyne. A striking feature is the complete absence of trimethylbenzene. Instead, we observe formation of benzene and a product detected at 82 amu, along with hydrogen, propene and a small amount of butadiene. Thus it appears that, instead of trimerising to C_9 trimethylbenzenes, two propyne molecules condense to yield C_6 species – either benzene or the 82 amu product.

Table 1 summarises product yields for a series of TPR experiments carried out with different initial propyne coverages (the propyne doses and XPS-derived initial coverage are both given). The relative yields of products, corrected for instrumental sensitivity factors, are shown as a function of initial propyne dose. In the case of the 82 amu product calibration experiments were not possible, so the uncorrected intensities are reported. The yields of propene and hydrogen are approximately independent of initial propyne coverage. The yields of benzene and the 82 amu product initially increase and then decrease with increasing propyne coverage, and butadiene is observed at only the lowest propene initial coverage. No trimethylbenzene formation was observed for any propyne initial coverage. On the basis that production of one molecule of either propene, benzene, or the 82 amu product (see below) requires consumption of one, two, and two molecules of propyne, respectively, we may use the data in table 1 to estimate that under conditions of maximum C_6 activity (0.5–2.0 L exposure) ∼25% of the initially adsorbed propyne undergoes conversion to gaseous products. Benzene formation from propyne implies hydrogen production, though a significant fraction of the H_2 undoubtedly comes from propyne decomposition (see below).

In order to investigate the possibility that trimethylbenzene *is* formed, but undergoes decomposition before desorption, the adsorption/desorption behaviour of 1,2,4-trimethylbenzene (120 amu) was studied. Figure 2 shows the 120 amu desorption spectrum obtained after saturating Cu{111} with 1,2,4-trimethylbenzene at ∼120 K. This adsorbate yields a desorption peak at ∼290 K with a shoulder

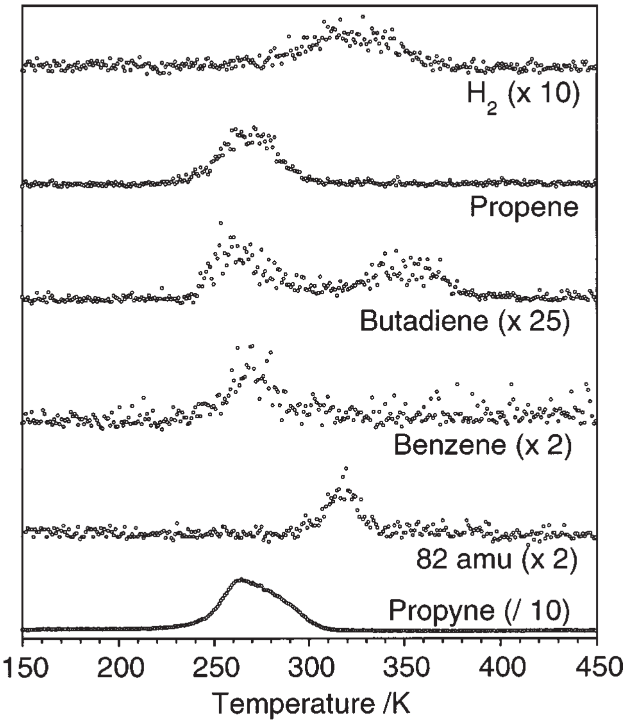


Figure 1. TPR spectra showing desorption of reactant and products after dosing 0.5 L (0.02 ML) propyne on Cu{111} at 120 K. All data (except 82 amu) corrected to allow for interferences resulting from mass spectrometer fragmentation and for mass spectrometer absolute sensitivities (see text).

Table 1
Relative desorption yields of reactant and products as a function of propyne dose.

Propyne exposure (L)	Propyne initial coverage (ML)	Propyne	Propene	Benzene	82 amu product[a]	Hydrogen	Butadiene	Propyne decomposition (%)
0.5	0.02	100 ± 3	10 ± 1	10 ± 1	8 ± 1	5 ± 1	4 ± 1	5
2.0	0.1	480 ± 6	30 ± 5	20 ± 5	25 ± 5	6 ± 1	Trace	4
5.0	0.22	1013 ± 9	90 ± 10	Trace	11 ± 8	17 ± 1	Trace	6
10.0	0.25	1098 ± 6	80 ± 10	None	None	13 ± 1	Trace	4

[a] Uncorrected raw data.

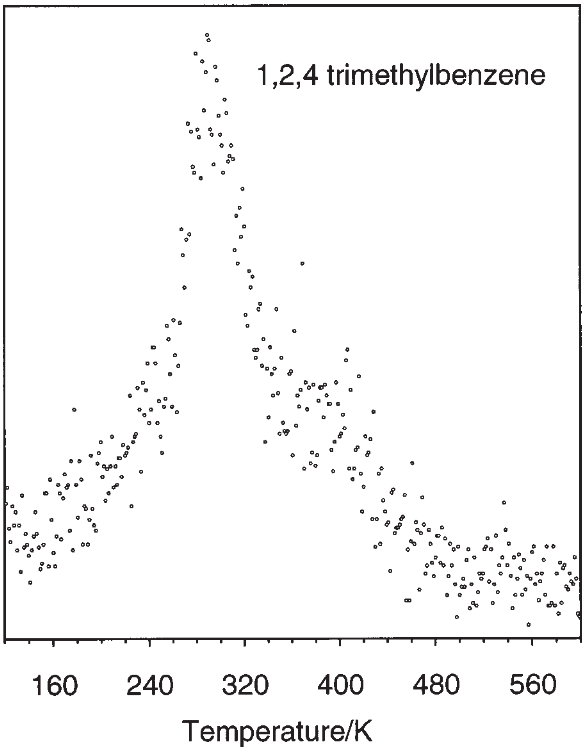


Figure 2. TPD spectrum showing desorption without decomposition of 1,2,4-trimethylbenzene from Cu{111}. Initial dose 10 L at ~120 K.

at ~395 K. No other products were found and no carbon deposition was detected by XPS. Thus trimethylbenzene desorbs from Cu{111} without significant decomposition.

In view of the reaction mechanism to be proposed below for benzene formation, it is possible that cyclohexene formation occurs, which species could then account for the product at 82 amu. (Cyclohexene to benzene conversion is known to occur [11] on silica-supported Cu catalysts.) Figure 3 shows TPR/TPD spectra obtained after saturating (5 L) the clean metal surface with cyclohexene at ~120 K. Unreacted cyclohexene exhibits a desorption rate maximum at ~195 K. This is accompanied by benzene formation ($T_p \approx 225$ K), but no production of cyclohexadienes. On the other hand, the 82 amu product resulting from reactions of propyne desorbs at 320 K (figure 1). This suggests, but does not prove unambiguously, that cyclohexene is *not* formed from propyne: the possibility remains that propyne to cyclohexene conversion is a surface reaction rate limited process rather than a desorption rate limited process. However, relative intensities in the mass spectrometric fragmentation pattern we determine for cyclohexene are as follows: 51 amu (1.3 ± 0.1), 54 amu (4.8 ± 0.6), 77 amu (0.61 ± 0.09), 78 amu (1.0 ± 0.1), 79 amu (0.53 ± 0.08), and 82 amu (1.5 ± 0.2). The corresponding values for the 82 amu species formed by reaction of propyne are very different and as follows (appropriate corrections having been made for intensity contributions from other relevant species): 51 amu (zero), 54 amu (zero), 77 amu (0.5 ± 0.3), 78 amu (1.0 ± 0.4), 79 amu (zero), and 82 amu (0.8 ± 0.3). Therefore, all the evidence indicates that cyclohexene is not produced during the reaction of propyne on Cu{111} and that the explanation for the 82 amu product must be sought elsewhere.

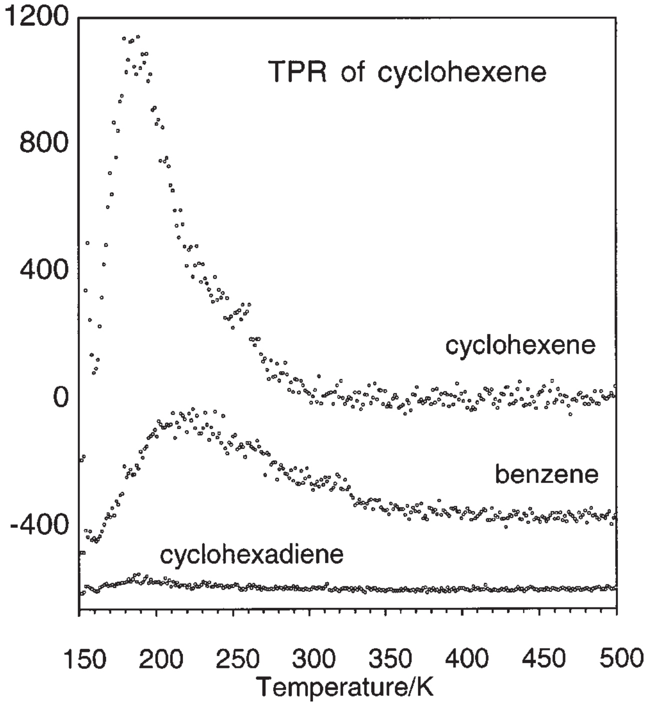
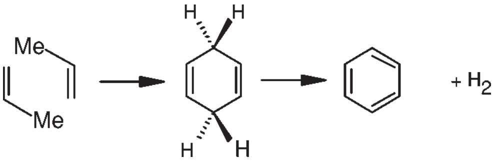


Figure 3. TPR spectra showing desorption and reaction of cyclohexene on Cu{111}. Initial dose ~5 L at ~120 K.



Scheme 1.

A plausible mechanism for propyne coupling to benzene could involve head-to-tail interaction of two propyne molecules with elimination of hydrogen, as indicated in scheme 1. The scheme is intended to depict two di-σ-adsorbed *propyne* molecules (not propene) with their methyl groups tilted towards each other. This direct mechanism is consistent with the observation that hydrogen desorption occurs after benzene formation (figure 1). Note that this scheme calls for no C–C bond cleavage and requires that hydrogen elimination should occur exclusively from the methyl groups. That is, 1,4-cyclohexadiene plays the role of reaction intermediate. An alternative and more complicated route would involve intramolecular H-transfer prior to aromatisation, i.e., conversion of 1,4- to 1,3-cyclohexadiene before hydrogen elimination and benzene formation.

To determine whether propyne coupling could proceed via cyclohexadiene intermediates, the reactivity of both 1,3- and 1,4-cyclohexadiene was examined. Both molecules do indeed yield benzene, hydrogen and no other products. The results are shown in figure 4: 1,3-cyclohexadiene generates benzene with rate maxima at ~185 and 240 K;

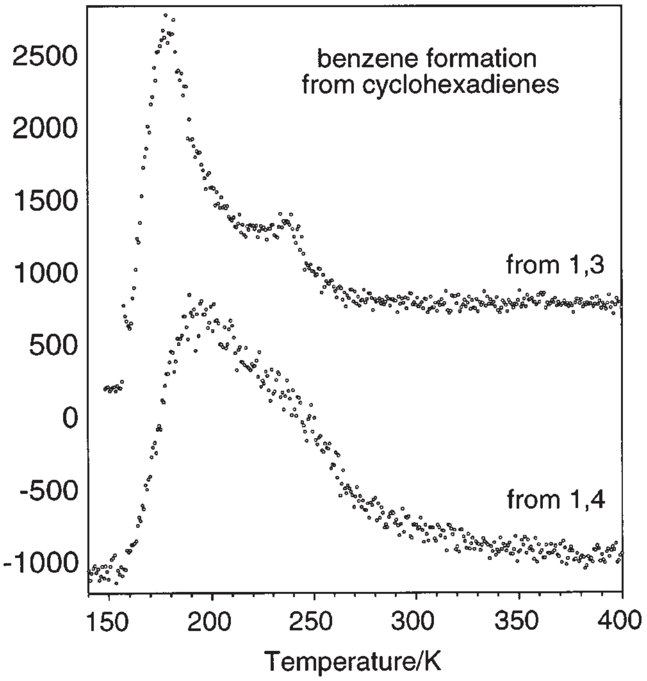
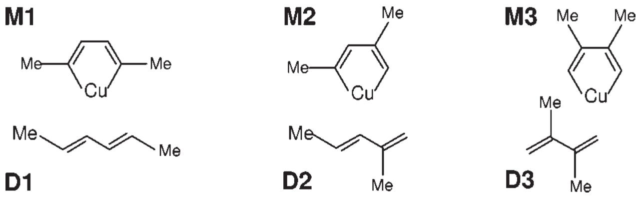


Figure 4. TPR spectra showing benzene formation from 1,3- and 1,4-cyclohexadienes on Cu{111}. Initial dose $\sim$5 L at $\sim$120 K.



Scheme 2.

1,4-cyclohexadiene gives a maximum at $\sim$195 K with a shoulder at $\sim$240 K. Thus both molecules could act as intermediates in the coupling of propyne to benzene. Since propyne coupling results in a benzene peak at the higher temperature of $\sim$270 K, the implication is that cyclohexadiene dehydrogenation is not the rate-limiting step in propyne $\rightarrow$ benzene conversion. Rather, it is the initial coupling reaction to form the cyclohexadiene(s) that is rate-determining, which seems plausible, given the relative complexity of this process.

Given recent work which shows that 1,4-cyclohexadiene is strongly preferred on Pt(111) and that 1,3-cyclohexadiene readily converts to the 1,4 isomer below room temperature [12,13], we suggest that in the present case propyne coupling via the more complicated 1,3-cyclohexadiene route seems unlikely.

To investigate whether propyne trimerisation is inhibited by the methyl group, we examined the possibility of reacting propyne with ethyne using a range of initial conditions. Efficient ethyne trimerisation to benzene occurred, but there was never any production of either methylbenzene or dimethylbenzenes.

The adsorption site, bonding and hybridisation of propyne on Cu{111} [14] as determined by photoelectron diffraction are essentially the same as those of ethyne on Pd{111} [8] and Cu{111} [9]. On Cu{111} both molecules form a $(\sqrt{3} \times 4)R30^\circ$ structure at saturation coverage, and the maximum packing density is similar in the two cases. The structural data show clearly that the C–C–C bond angle for propyne/Cu{111} is 120° indicating sp^2 hybridisation and a di-σ-adsorbed molecule. Yet ethyne trimerises with high efficiency and propyne not at all. Instead, two molecules of propyne couple to form benzene with elimination of hydrogen, accompanied by an approximately equal amount of the 82 amu species and certain other products that we shall also discuss. Given the similar adsorption structures of ethyne and propyne, the failure of propyne to trimerise is unlikely to be due to insufficiently close approach of the molecules. Other factors must be at work. In accord with this view, coadsorption of propyne with ethyne generated neither methylbenzene nor dimethylbenzenes. The absence of methylbenzene production in these experiments indicates that a propyne molecule cannot couple with the C_4H_4 intermediate that is produced efficiently from ethyne [1,6]. Does the absence of *dimethylbenzene* point to the failure of two propyne molecules to couple to the dimethyl-metallopentacycle analogous to C_4H_4?

When ethyne alone reacts on Cu{111} to form benzene via the C_4H_4 intermediate, butadiene is formed in a side reaction by hydrogenation of the C_4H_4 intermediate [6]; similar behaviour is found on Cu(110) [1]. Should the analogous dimerisation reaction occur in the case of propyne, hydrogenation of the resulting dimethyl-metallopentacycle intermediate would yield *a diene of mass 82 amu.* This would account in a natural way for the 82 amu product. Three possible diene species can be formed, resulting from hydrogenation of the three different possible dimethyl-metallopentacycle isomers, as illustrated in scheme 2. That is, propyne *can* dimerise, but incorporation of a third propyne molecule to yield trimethylbenzenes is hindered and does not occur.

Both benzene production and diene production are quenched as the initial coverage of propyne approaches the saturation value. This may reflect a requirement for adsorbate mobility in order for these reactions to occur; such mobility may become restricted as the overlayer becomes denser. Alternatively, it could be that the adsorbate forms islands at all coverages (as does ethyne on Pd{111}) with reaction occurring at island edges. However, the LEED data do not give any indication of island formation at low coverages so that the first interpretation seems more likely.

Consider the production of hydrogen and propene. Each benzene molecule formed generates two H_a. Each propyne molecule formed consumes two H_a. However, propene production always exceeds benzene production by at least a factor of two. In addition, formation of the 82 amu dienes implies additional consumption of H_a. Therefore, there must be an additional source of H_a in addition to benzene production. The obvious candidate is propyne decomposition to $C_a + 4H_a$. We may estimate the amount of propyne that undergoes decomposition by making use of the following relationship between the various yields:

$$\begin{aligned}&\text{benzene} + 2 \times (\text{propyne decomposed})\\&\quad = \text{propene} + \text{hydrogen} + 82\ \text{amu product}\end{aligned}$$

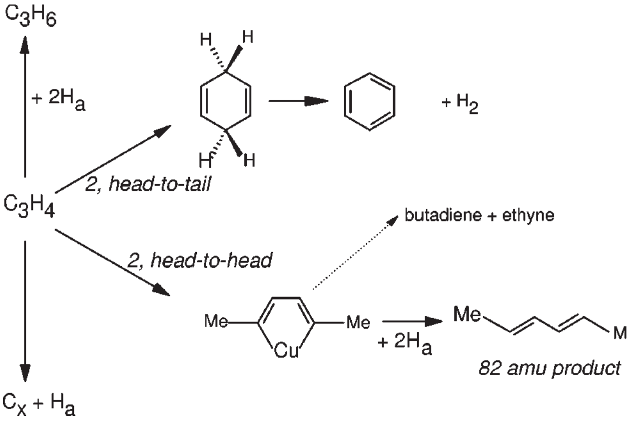
Of course, we have no sensitivity calibration factor for the 82 amu species, so in the above relationship we can use only the raw data: the error introduced is not large, and the results are summarised in figure 1. It appears that propyne decomposition amounts to ~5% of the initial coverage.

Finally, we need to explain for the formation of butadiene, which appears only at the lowest coverages: how does one generate a C_4 product from a C_3 reactant? In principle, one might account for this by a sequence of the type

$$\begin{aligned}&2C_3(\text{propyne})\\&\quad \rightarrow C_6(\text{dimethyl-metallopentacycle intermediate})\\&\quad \rightarrow C_4(\text{butadiene}) + C_2(\text{ethyne})\end{aligned}$$

The first step is consistent with formation of the 82 amu dienes and the overall scheme has the correct stoichiometry. Interestingly, the second step is only feasible for only one of the three possible dimethyl-metallopentacycle intermediates, namely that labelled M1 in scheme 2. It involves scission of one C–C bond and two intramolecular hydrogen transfers. Such a process may be favoured at lower adsorbate coverages because of (i) the availability of necessary vacant Cu sites, and/or (ii) the relatively low concentration of H_a which favours the competing hydrogenation of the intermediate to form the 82 amu product. Notice that M1 corresponds to a head-to-head interaction, as does M3; however, the latter cannot yield ethyne and butadiene without a methyl group shift. M2 corresponds to a head-to-tail interaction. This leads to the following attractive explanation for the observed coupling chemistry of propyne on Cu(111). Head-to-tail interaction leads to benzene formation. The two sp^2 hybridised molecules can tilt towards each other, hydrogen transfer occurs, forming 1,4-cyclohexadiene, followed by hydrogen elimination and benzene formation (scheme 1). Head-to-head interaction cannot achieve this because of steric interference between adjacent methyl groups. Instead, coupling to form metallocycles M1 and M3 occurs, leading ultimately to the 82 amu dienes D1 and D3, with co-production of a small amount of butadiene and ethyne as a result of some rearrangement and hydrogenolysis of M1, as discussed above. An overall reaction network that accounts for all the observed products may then be proposed, as shown in scheme 3. This corresponds to the simplest interpretation with the minimum number of reactions.

Finally, it is interesting to note that on Cu{110} some trimerisation of propyne does occur, but no benzene production was reported. In that case [15], RAIRS data indicated the presence of di-σ/di-π-adsorbed propyne, in contrast with the sp^2 di-σ-adsorbed species present on Cu{111}. It thus appears that the coupling chemistry of propyne on copper surfaces exhibits very pronounced structure sensitivity.



Scheme 3.

4. Conclusions

1. The chemistry of propyne on Cu{111} is very different from that of ethyne. The overall reactivity of propyne is substantially lower and trimerisation does not occur. Instead, *either* two propyne molecules couple with elimination of hydrogen to yield benzene, *or* they couple to form a metallocycle which hydrogenates to yield C_6 dienes.

2. A plausible mechanism for benzene formation involves head-to-tail interaction of two propyne molecules. Cyclohexadienes are possible intermediates in this process, their formation being rate determining.

3. It appears that propyne trimerisation is sterically inhibited by the methyl group. However, the first stage in this process, namely formation of a dimethyl-metallopentacycle intermediate, does seem to occur. This may be ascribed to head-to-head coupling of two propyne molecules. The metallocycle is unable to add a third propyne (or ethyne) molecule. Instead, it undergoes either hydrogenation (to C_6 dienes) or disproportionation to butadiene and ethyne.

4. Approximately 5% of the initial propyne overlayer undergoes decomposition leading to formation of propene and some hydrogen.

Acknowledgement

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