

A Theoretical Study of Catalytic Coupling of Propyne on Cu{111}

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Received February 17, 2000

Abstract: The coupling mechanism of two propyne molecules on the Cu{111} surface has been studied by means of a DFT cluster model approach. The gas-phase dimerization is highly unfavored because of the energy cost to activate propyne by promoting molecules to the triplet state. However, on the surface, propyne is adsorbed with a geometry very close to that of gas-phase propyne in the triplet state and, therefore, activation of the reacting molecules does not incur any additional energy cost. Moreover, isomerization to vinylcarbene is necessary to allow head-to-tail or head-to-head coupling resulting in 1,4- and 1,3-cyclohexadiene intermediates. Vinylcarbene biradicals are present at the surface because the isomerization process proceeds at practically no (thermodynamic) cost. Both head-to-tail and head-to-head interactions suggested by experiment are possible. Both cyclohexadiene intermediates can dehydrogenate to yield benzene and H₂ with a moderate energy cost. An alternative head-to-head interaction, without interacting tails, yields two C₆ noncyclic intermediates which, upon H₂ addition, can be regarded as being responsible for the 82 amu product observed in the reaction.

I. Introduction

It has been recently reported that the coupling reactions of propyne on Cu(111) are very different from those exhibited by ethyne (acetylene).¹ Ethyne on various metals surfaces (Cu, Pd, and Pd/Au) is known to trimerize to benzene through a molecular mechanism involving a C₄H₄ intermediate.^{2,3} This intermediate is formed by coupling two ethyne molecules, and subsequent reaction with a third ethyne molecule ultimately leads to benzene. The efficiency of the trimerization process is rather high, ranging from ~60% on Pd(111) to ~80% on Pd/Au surfaces, and reaching almost complete stoichiometric conversion to benzene on Cu(110) and Cu(111) even at low temperatures.⁴ For propyne on Cu(111) the analogous process would lead to 1,2,4- and 1,3,5-trimethylbenzene. Indeed, these products of trimerization are observed when propyne reacts on TiO₂{001}.⁵ One might therefore expect the same reactions occur on Cu(111). However, recent experimental work by Middleton and Lambert^{1,4} has shown that, contrary to the case of ethyne, propyne does not trimerize on Cu{111}. In fact, the catalytic chemistry of propyne on Cu{111} is very different (see Figure 1). No trimerization occurs and the principal reaction products are benzene, H₂, and a product detected by mass

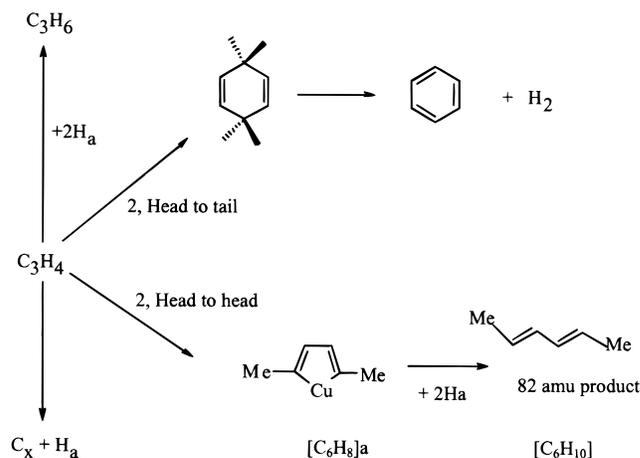


Figure 1. Schematic representation of the propyne coupling mechanism suggested in ref 1.

spectroscopy at 82 atomic mass units (amu), which corresponds to an unsaturated C₆H₁₀ molecular formula. It was argued¹ that this 82 amu product could be 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-pentadiene, and 2,4-hexadiene, only the latter being depicted in Figure 1. Furthermore, when adsorbed propyne is co-coupled with adsorbed ethyne on Cu{111}, benzene is the only product,¹ resulting from ethyne trimerization and from the coupling of two propyne molecules. Methylbenzene and dimethylbenzenes are not formed. Therefore on Cu{111} an entirely different mechanism must operate in the case of propyne, which strongly favors the C₆ coupling product rather than the C₉ trimerization product. A possible mechanism for the propyne reaction involving head-to-tail coupling of two propyne molecules has been proposed,¹ Figure 1. That is, the

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approach of the CH group (head) of one molecule toward the end (tail) of the other and the tail of the former to the head of the last. This mechanism could lead to formation of a cyclohexadiene intermediate, followed by H₂ elimination to yield benzene. A head-to-head, without interacting tails, mechanism is also possible and it is suggested that this alternative mode of interaction is responsible for the 82 amu product. The first stage of this process is formation of a dimethyl-metallopentacycle. However, this metallocycle cannot add a third propyne molecule and instead undergoes other reactions such as hydrogenation to C₆ dienes.

The mechanism outlined in Figure 1 accounts for most of the experimental observations although it is by no means intended to suggest detailed elementary steps. In fact, the direct approach of two propyne molecules to form the 1,3-cyclohexadiene molecule involves the concerted transfer of two hydrogen atoms. Such a concerted process is rather unlikely and the reaction probably proceeds via a sequence of elementary steps. Moreover, it is quite clear that the interacting molecules need to be distorted from the linearity imposed by the triple bond for cyclization to benzene to occur. For ethyne trimerization on Pd(111), the interplay of theory and experiment confirmed the proposed mechanism.⁶ In particular, the theoretical analysis of the vibrational frequencies of a C₄H₄ intermediate adsorbed on a surface cluster model corroborated the assignment of frequencies on the HREELS spectrum to this intermediate, thus supporting the proposed catalytic mechanism. Therefore, use of theoretical models should be of value in elucidating the mechanism of propyne coupling: this is the aim of the present work. To this end we have performed first principles Density Functional Theory, DFT, cluster model calculations for the various species involved in the coupling mechanism. The present approach starts with a study of the gas-phase reaction which allows us to identify some key features of the process, in particular, the requirement for a highly distorted geometry in the reacting propyne molecules and the possibility of an alternative pathway via vinylcarbene (although vinylcarbene will be used to refer to this radical we must point out that strictly speaking one should refer to this species as biradical propene-1,3-diy). The study of these gas-phase reactions provides a better understanding of the role played by the surface. Next, we describe the adsorption properties, geometry, and energy of adsorbed propyne and vinylcarbene; finally, the different coupling mechanisms of two adsorbed propyne molecules are discussed.

II. Computational Details

For the gas-phase reaction between two propyne molecules (or two propyne derived biradical species) ab initio all electron DFT calculations have been carried out within the B3LYP^{7,8} model for the exchange-correlation functional and the standard 3-21G⁹ Gaussian basis set. The aim of these calculations is to explore the different reaction paths and more specifically the thermodynamic feasibility of the gas-phase reaction. To this end, B3LYP calculations have been carried out to obtain the optimum geometry and energy of propyne and of the vinylcarbene biradical. Both singlet and triplet multiplicities have been considered for propyne, whereas for the vinylcarbene biradical only the triplet state was considered, to avoid difficulties connected with the description of open shell singlets by means of a single Kohn-Sham determinant. The purpose of these calculations is not to provide

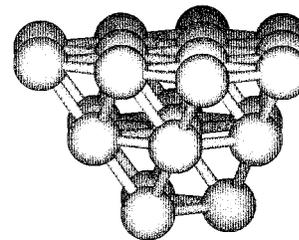


Figure 2. The Cu₂₂(12,7,3) cluster model used to represent Cu{111}.

a detailed study of the gas-phase reaction including transition state geometry and energy but rather to analyze the key features of this process.

Chemisorption of propyne and vinylcarbene on Cu{111} has been studied by means of the cluster model approach.^{10–12} The Cu{111} surface has been modeled by a Cu₂₂(12,7,3) cluster model, Figure 2. This cluster is a section of the ideal Cu{111} surface with a Cu–Cu nearest neighbor distance taken from the bulk and equal to 2.551 Å; the cluster geometry has been held fixed in all subsequent calculations involving adsorbate geometry optimization. Following previous work, this cluster is divided into two regions which are treated in a different way.¹³ The *local* region is defined by the three most internal atoms of the surface layer whereas the rest of the atoms define the *outer* region. Atoms in the *local* region are described by a relativistic, small core, effective core potential, ECP, which treats explicitly the 3s²3p⁶3d¹⁰4s¹ valence electrons of each Cu atom;¹⁴ these electrons are described by the standard, LANL2DZ, double- ζ basis set of Hay and Wadt also taken from ref 14. The remaining cluster atoms are described with a more extended ECP that leaves just one 4s valence electron per Cu atom¹⁵ and a minimal basis set. This constrained description of the system is imposed by the necessity of performing a full geometry optimization of adsorbed propyne and vinylcarbene geometry in the absence of symmetry elements. The determination of the geometry of the cyclohexadiene structures arising from the head-to-tail, HT, and head-to-head, HH, mechanisms is computationally even more demanding. On the other hand, basis set requirements on DFT calculations are less stringent than those concerning ab initio wave function based methods. Therefore, the present calculations are thought to provide a semiquantitative view of the various reaction paths rather than an exhaustive and quantitative description of the energy of each elementary step.

All calculations were carried out using the Gaussian-94 suite of quantum chemical computational programs.¹⁶

III. Gas-Phase Dimerization of Propyne

The coupling of two propyne molecules requires distortion from the linear geometry of the isolated molecule imposed by the carbon–carbon triple bond. Two possible ways to activate propyne are considered. The first is a promotion to the first triplet state, whereas the second involves an intramolecular hydrogen transfer to form vinylcarbene, a biradical species,

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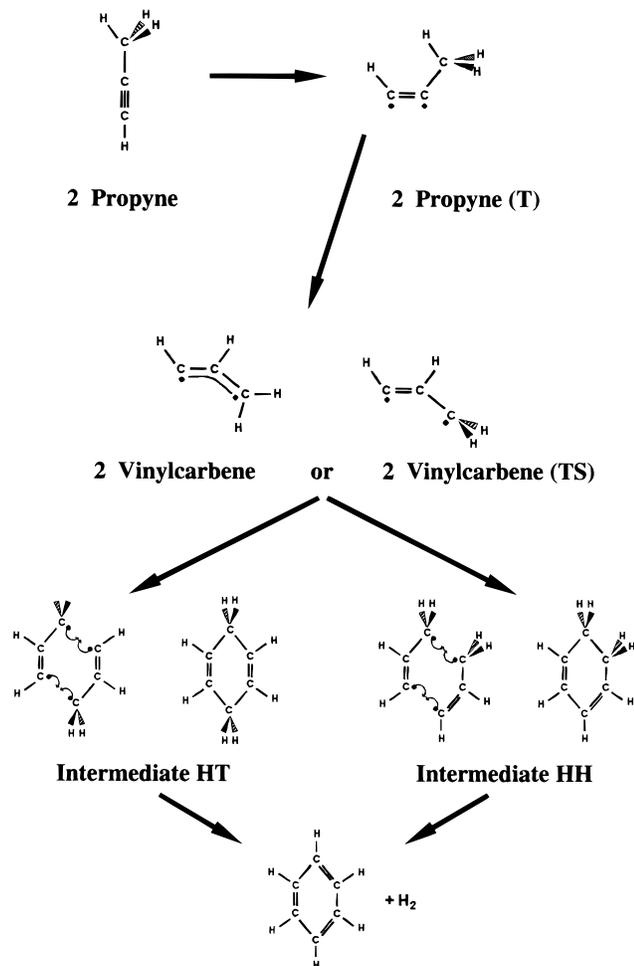


Figure 3. Schematic representation of the reaction gas-phase reaction path involving coupling of two propyne molecules.

Figure 3. Both triplet propyne and triplet vinylcarbene can be HT or HH coupled to yield 1,3- and 1,4-cyclohexadiene, which after H₂ elimination lead to benzene. A schematic representation of this gas-phase mechanism is presented in Figure 3. The hypothesis of the vinylcarbene biradical arises naturally from the need to avoid a double hydrogen transfer, in one or two steps, to obtain the cyclohexadiene species by direct coupling of two triplet propyne molecules.

The geometries of some of the species involved in the reaction pathway indicated in Figure 3 are of interest because, as will be shown later, they are closely related to the structure of these same species adsorbed on Cu{111}. The 3-21G/B3LYP geometry of the carbon chain of gas-phase propyne in its closed shell electronic ground state is linear, as expected, whereas that corresponding to the triplet is highly deformed with the three carbon atoms forming an angle of 130°, Figure 4. Also indicated in Figure 4 is the optimized geometry of the triplet vinylcarbene biradical. Optimization of the geometry in the closed shell singlet state yields cyclopropene and the open shell singlet has not been considered because (i) the singlet–triplet difference is not significant within the scope of the present work and (ii) the proper description of the open shell singlet requires more than one Slater determinant, and cannot be currently treated in the Kohn–Sham implementation of DFT. For the biradical, a nonplanar structure is also obtained, but this corresponds to a transition state involving rotation of the methylene group along the C–CH₂ axis with a barrier of 0.82 eV.

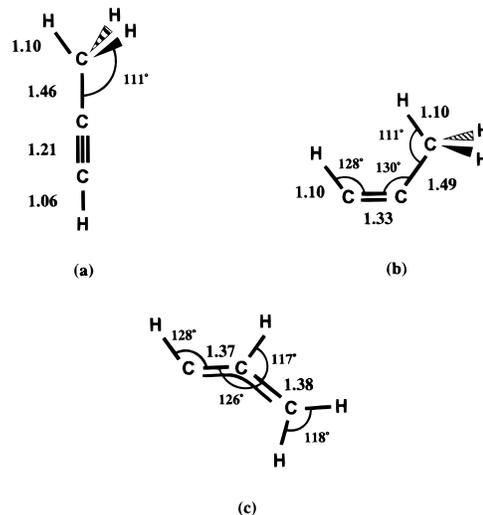


Figure 4. Schematic representation of the optimized geometry of gas-phase propyne, singlet (a) and triplet (b), and vinylcarbene, triplet (c).

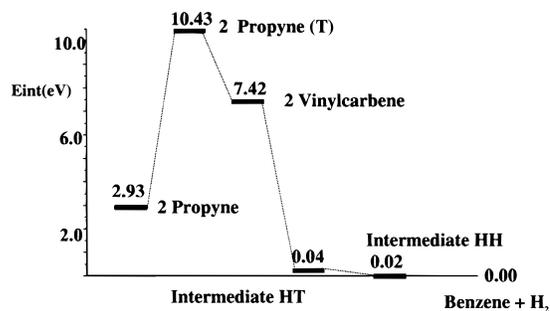


Figure 5. Schematic energy profile of the gas-phase reaction depicted in Figure 3.

The energy necessary to promote propyne from the singlet to the triplet state at the 3-21G/B3LYP level of theory is quite high, 3.75 eV, and well above the energy of the vinylcarbene biradical which lies 2.25 eV above the ground-state structure. However, once propyne triplet or vinylcarbene are formed, both the HT and HH couplings are rather favorable processes. Moreover, the energy of these intermediates is only 0.04 or 0.02 eV above the energy corresponding to benzene plus H₂; a schematic representation of this energy profile is given in Figure 5. From this energy profile it is clear that while the coupling reaction is thermodynamically favorable, the formation of the intermediate precursors requires very high energies so that the process is hindered. The study of the gas-phase reaction also shows that once propyne is activated the coupling reaction is highly exothermic. The fact that the reaction occurs with very low activation energy on the Cu{111} surface¹ indicates that the role of the surface is to activate the propyne molecule at a low-energy cost. Results presented below show that this is indeed the case, and that the geometry of adsorbed propyne is close to that corresponding to the triplet state of gas-phase propyne.

IV. Propyne Coupling on the Cu{111} Surface

The optimized structure of propyne (singlet state) on the Cu₂₂ cluster model used to represent the Cu{111} surface exhibits some important features, Figure 6. In particular, it closely resembles the structure of chemisorbed ethyne.¹⁷ Interaction with the surface destroys the linearity imposed by the triple bond,

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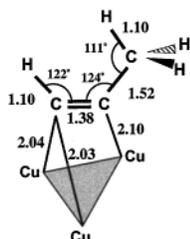
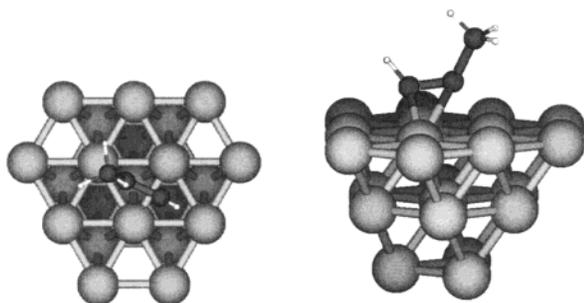


Figure 6. Top and side view of the optimized geometry of propyne adsorbed on Cu{111}; the relevant distances (Å) and angles (deg) are schematically shown at the bottom of the figure.

the molecule is strongly bent, and the main interaction involves atoms in the local region of the cluster surface model. The close agreement between the present calculated, 124° , and experimental (photoelectron diffraction), 120° ,¹⁸ C–C–C bond angle for chemisorbed propyne indicates that the present approach is a reliable one. More importantly, the observed geometry of chemisorbed propyne is remarkably close to that obtained for the gas-phase propyne in the triplet state: compare the geometries indicated in Figure 4 and Figure 6. With the present model and method, the adsorption of propyne is slightly exothermic, -0.22 eV, thus below the energy of Cu₂₂ plus propyne. This interaction energy can be viewed in a two-step process,^{17,19} the cost to distort propyne to activate the molecule, $+3.24$ eV, and the gain obtained by allowing this *activated* molecule to interact with the surface, -3.46 eV. This is because the distortion of the singlet is less important than that to obtain the optimized geometry of the triplet (for the same structure, the biradical singlet should be above in energy).

Now, let us consider the chemisorption of the vinylcarbene biradical. In this case the gas-phase molecule is already distorted from the linear geometry and ready to interact with the substrate but the interaction with the surface induces noticeable changes in the structure, Figure 7. Nevertheless, the interaction energy is quite large and the geometry of the adsorbed biradical is similar to that of the gas-phase species, except for the tilting of the hydrogen atoms of the methylene group toward the vacuum, to decrease the Pauli repulsion with the surface. The interaction energy with the surface is large, -2.70 eV, and it is even larger if one considers the energy cost to distort the geometry of the biradical from that corresponding to the gas phase, $+1.43$ eV. Hence, the interaction energy with respect to the hypothetical *activated* vinylcarbene is -4.13 eV. Taking into account the energy necessary to obtain the biradical from propyne, $+2.25$ eV, the interaction energy with respect to gas-phase propyne plus Cu₂₂ is -0.45 eV. Therefore, it is very possible that adsorbed propyne spontaneously isomerizes to adsorbed vinylcarbene at finite temperatures.

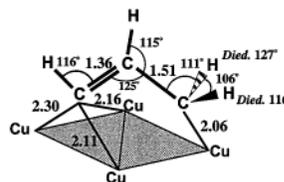
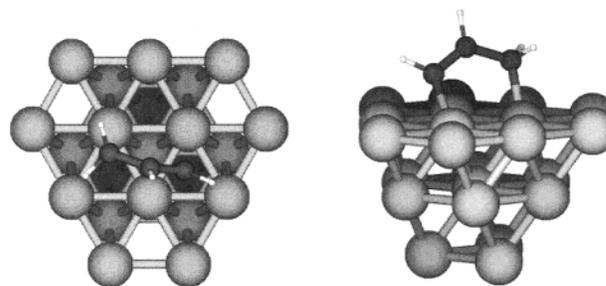


Figure 7. Top and side view of the optimized geometry of vinylcarbene adsorbed on Cu{111}; the relevant distances (Å) and angles (deg) are schematically shown at the bottom of the figure.

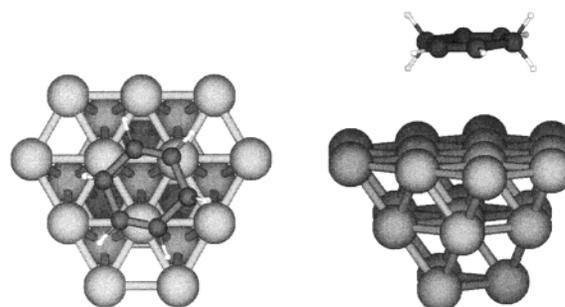


Figure 8. Top and side view of the optimized geometry of the head-to-tail, HT, 1,4-cyclohexadiene intermediate arising from the coupling of two vinylcarbene species adsorbed on Cu{111}.

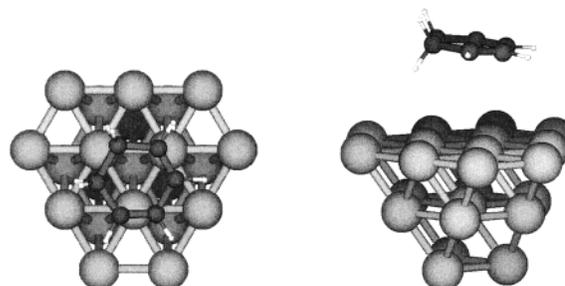


Figure 9. Top and side view of the optimized geometry of the head-to-head, HH, intermediate arising from the coupling of two vinylcarbene species adsorbed on Cu{111}.

Having obtained the structures of isolated chemisorbed propyne and vinylcarbene species, calculations were carried out for a pair of these species on the model surface, in both HT and HH orientations. The resulting chemisorbed structures are of course larger than the single species and extend somewhat beyond the local region. This may introduce some uncertainty in the calculated energies, but we do not expect that qualitative changes in the structures or energy profile would result from the use of a larger local region. Such calculations are beyond our present computing facilities. For the HT and HH coupling mechanism involving two vinylcarbene radicals the optimization geometries lead to 1,4-, Figure 8, and 1,3-cyclohexadiene, Figure 9, intermediates suggested by Middleton and Lambert, Figure 1. Both cyclohexadienes are stable on the Cu₂₂ cluster model

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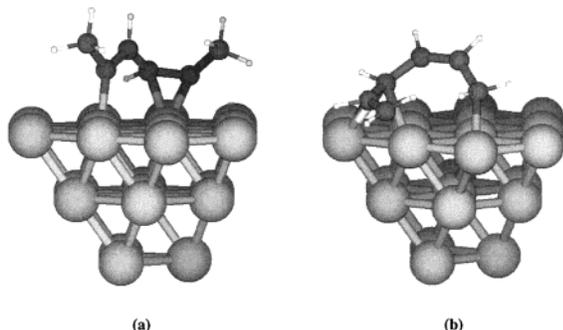


Figure 10. Side view of the C₆ intermediates obtained from HH coupling of either two adsorbed propyne (a) or two adsorbed vinylcarbene species (b).

of Cu{111}, with the 1,4-isomer more stable than the 1,3-isomer, in agreement with experimental evidence.¹ Both intermediates are stable with respect to dissociation to gas-phase benzene plus H₂, by 0.51 and 0.46 eV, respectively. Therefore, the energy cost to transform to the final products is relatively low so that the reaction may be expected to occur under experimental conditions (<200 K). The energy cost required to obtain the final products from the cyclohexadiene intermediates is consistent with the relatively low conversion of propyne to benzene on Cu{111}, ~10% of the initial propyne overlayer.¹ Moreover, cyclohexadiene intermediates could be hydrogenated to cyclohexene, which is also a 82 amu product. The identity of cyclohexene as the 82 amu product was rejected because the desorption profile and mass spectral fragmentation pattern of cyclohexene are very different from that of the 82 amu product.

Additional calculations were carried out starting the geometry optimization procedure of either two propynes or two vinylcarbenes but only interacting by an extreme of each molecule. HH, HT, and TT couplings are all possible. These adsorbed noncyclic-C₆ intermediates could yield some 82 amu products after hydrogenation. Both propyne and vinylcarbene HH coupling would produce 2,4-hexadiene. Propyne TT and HT coupling would generate nonlinear dienes, 2,3-dimethyl-1,3-butadiene and 2-methyl-1,3-pentadiene, respectively. Vinylcarbene TT and HT coupling would yield linear dienes, 1,5-hexadiene and 1,4-hexadiene, respectively. Among these six possibilities, only the corresponding HH coupling intermediates are obtained in the minimization process. These adsorbed C₆H₈ intermediates are schematically reported in Figure 10. The existence of these two adsorbed species adds further support to the suggestion of 2,4-hexadiene as the resulting hydrogenated 82 amu product. In addition, this is also in agreement with the mechanism suggested by Middleton and Lambert.¹ These adsorbed C₆ noncyclic species are considerably more stable than two adsorbed isolated propyne or vinylcarbene molecules, although they are energetically less favored than the HT and HH cyclohexadiene intermediates.

A rather complete picture of the coupling reaction thus emerges, at least from a thermodynamic point of view. A schematic representation of the energy profile is presented in Figure 11. From this profile it is clear that the highest energy corresponds to the reactants, two propyne molecules plus the surface cluster model, and that every subsequent process lowers the energy. The adsorption of two noninteracting propynes lowers the energy by 0.5 eV, transformation to two noninteracting vinylcarbene represents an additional gain of ~0.5 eV, and HT or HH interaction of these biradicals decreases the energy by almost 2.5 eV resulting in rather stable adsorbed

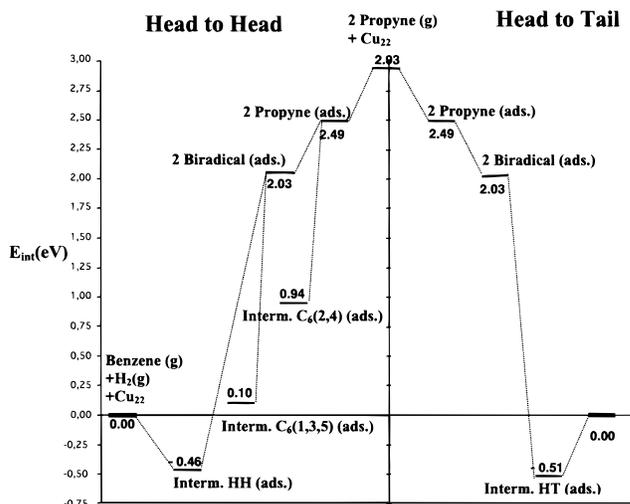


Figure 11. Schematic energy profile for the head-to-head and head-to-tail mechanisms for propyne coupling on the Cu{111} surface.

cyclohexadiene that can decompose to benzene and hydrogen without a large energy cost.

V. Summary

The coupling mechanism of two propyne molecules on Cu{111} has been studied by means of a DFT cluster model approach. The gas-phase reaction has also been studied. It is shown that the gas-phase reaction reveals key features of the surface-catalyzed process. The results provide a rather complete view of the coupling mechanism and lend further support to the mechanism suggested by Middleton and Lambert,¹ with some minor modifications, mainly involving participation of the vinylcarbene biradical species. This biradical appears in a natural way when the same coupling reaction is studied in the gas phase (vide infra). The gas-phase dimerization process is highly disfavored by the energy cost required to promote propyne to the triplet state. Moreover, isomerization to vinylcarbene is necessary to allow head-to-tail or head-to-head coupling resulting in 1,4- and 1,3-cyclohexadiene intermediates. On the Cu surface, propyne is adsorbed in a geometry very close to that of gas-phase propyne in the triplet state and, therefore, activation of the reacting molecules does not incur any additional energy cost. In addition, vinylcarbene biradicals may form at the surface because the isomerization process proceeds (thermodynamically) with no additional energy cost. Both head-to-tail and head-to-head interactions suggested in ref 1 are possible. Both interactions readily lead to cyclohexadiene (1,4-cyclohexadiene and 1,3-cyclohexadiene) which can dehydrogenate to yield benzene and H₂ at moderate energy cost. Moreover, cyclohexadiene can hydrogenate to cyclohexene which is a 82 amu species, but this possibility was rejected because the desorption profile and mass spectral fragmentation pattern of cyclohexene are very different from that of the 82 amu product. In addition, head-to-head (without interacting tails) interaction yields two C₆ noncyclic intermediates which, upon addition of adsorbed hydrogen, result in the experimentally observed 82 amu product (2,4-hexadiene).

The present study focuses on the energy profiles calculated by means of a cluster model and is not free from computational and physical limitations. While improving the level of calculation may lead to some variations in the energy profile, it is most unlikely that qualitative changes would result. A complete description of the reaction requires determination of the various

isomers and transition state structures, as well as the energy barriers between the different steps. Adsorbed structures other than propyne and vinylcarbene are not totally excluded. In this respect, propyne exhibits a much richer surface chemistry than ethyne and other mechanisms are possible, at least in principle. The study of the various isomers of chemisorbed propyne and their characteristic vibrational modes and intensities is beyond the scope of the present work and will be reported elsewhere.²⁰ However the computational burden necessary to obtain transition state structures greatly exceeds our present computational capabilities. The present study provides strong support for the mechanism suggested by experiment. It also enables us to illuminate additional key features of the mechanism thus providing a satisfactory and plausible account of a complex and

(20) Clotet, A.; Ricart, J. M.; Illas F.; Pacchioni, G. In preparation.

interesting heterogeneously catalyzed reaction that has many analogies in homogeneous catalysis.²¹

Acknowledgment. The authors acknowledge financial support from Spanish CICYT PB98-1216-C02 (01 and 02), Italo-Spanish HI1998-0042, and Catalan 1999SGR00182, 1999SGR00040, projects. Part of the computer time was provided by the CESCA/CEPBA supercomputer centers through a UB grant and through European ERB FMGE CT95 0062 TMR contract.

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