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On the mechanism of CuCl mediated amine addition to diacetylenes

G. Huerta, L. Fomina *

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, CU, Coyoacan, 04510, Mexico, DF, Mexico

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Abstract

A mechanism of CuCl mediated amine addition to diacetylenes resulting in pyrrole formation has been studied theoretically at B3LYP/6-31G* level of theory. The reaction proceeds via formation of Cu-stabilized carbene intermediates and the formation of the first intermediate is the rate determining reaction step. The catalytic action of CuCl is due to the reduction of activation energy of the carbene intermediate formation from 75.0 to 50.1 kcal/mol. The decrease in activation energy is related to the reduction of HOMO–LUMO energy gap between nucleophile and electrophile due to complex formation allowing to catalogue this reaction as interaction between soft acid and base.

Keywords: Copper chloride; Diacetylenes; Pyrroles

1. Introduction

The addition of primary amines to a 1,3-dyines resulting in substituted pyrrole formation, which is catalyzed by Cu [1] and Ti [2] salts is one of the important routes to substituted pyrroles and has been widely used to prepare a number of no symmetrical and symmetrical 2,5-disubstituted pyrroles. The mechanism of pyrrole formation is not clear. Probably the reaction sequence consists of the hydroamination and subsequent 5-*endo* cyclization, however, no clear evidences for one mechanism or another have been documented yet. The need for the catalysis is evident since, when the addition of benzylamine to 1, 4-diphenyl-1, 3-butadiyne is carried out in the absence of the copper salts, the major product is the 2, 3, 6-triphenylpyridine, instead of the 1, 2, 5,-triphenylpyrrole [3] (Scheme 1). Even using catalyst the reaction takes place at 160 °C–170 °C implying rather high activation energy [4, 5].

The aim of this paper is to obtain deeper insight into the mechanism of the reaction of diacetylene- amines using quantum chemistry tools to understand the effect of Cu(I) salts on the reaction mechanism.

2. Theoretical approach

As a model reaction the reaction between ammonia molecule and diacetylene (DA) has been selected. This model is the simplest possible yet maintaining all features of the real systems allowing complete and efficient potential energy scan to study all possible reaction routes and intermediates. All calculations were carried out with Jaguar v 6.0 program [6]. The geometry optimizations were run using hybrid B3LYP functional without any symmetry restrictions at B3LYP/6-31G* level of theory which is successful for modeling of organic molecules [7]. LAC effective core potential [8] was used to describe Cu atom. Actually, B3LYP functional was successfully applied to model Cu-mediated reactions [9]. Frequency calculations were run for all structures to make sure that a transition state (one imaginary mode) or a minimum (zero imaginary modes) is located and to obtain free Gibbs energies of reaction intermediates. First, the potential energy scan of ammonia-DA system was carried out to locate all stationary points on the way from starting materials to product (pyrrole). Then, similar procedure was repeated with ammonia -DA-CuCl system to find out possible mechanisms of catalytic action of CuCl. Poisson–Boltzman solver [10,11] implemented in Jaguar v 6.0 was used to calculate the solvation effects on the studied molecules in dimethylformamide (DMF) at the same level of theory. In other words, the structures have not been reoptimized in the presence of solvent since it has been shown previously that reoptimization has very limited effect on the computed energies [12–16].

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* Corresponding author. Tel.: +52 55 5 622 47 27; fax: +52 55 5 616 12 01.
E-mail address: lioud@servidor.unam.mx (L. Fomina).

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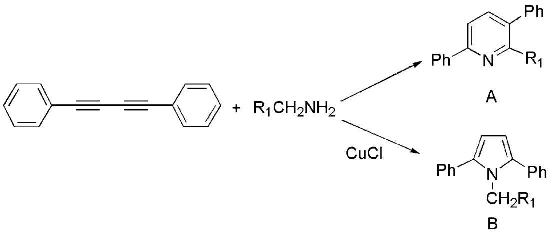
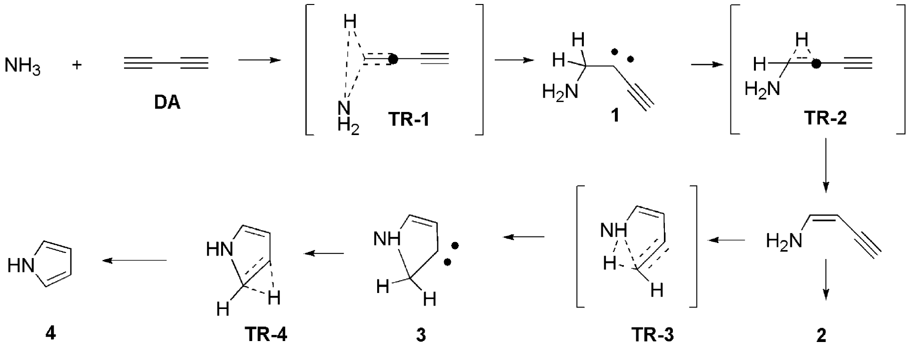


Scheme 1. Reaction of diphenyldiacetylene with amines.

3. Results and Discussion

The first step of the reaction mechanism is a nucleophilic addition of ammonia molecule to the triple bond of DA molecule (Scheme 2). Potential energy scan along C–N distance shows that the first minimum on the way to pyrrole is intermediate **1** preceded by a transition state TR-1. As seen from the reaction energy profile (Fig. 1) this step is the rate limiting step of the reaction mechanism with the free



Scheme 2. Catalyst-free reaction mechanism of pyrrole formation.

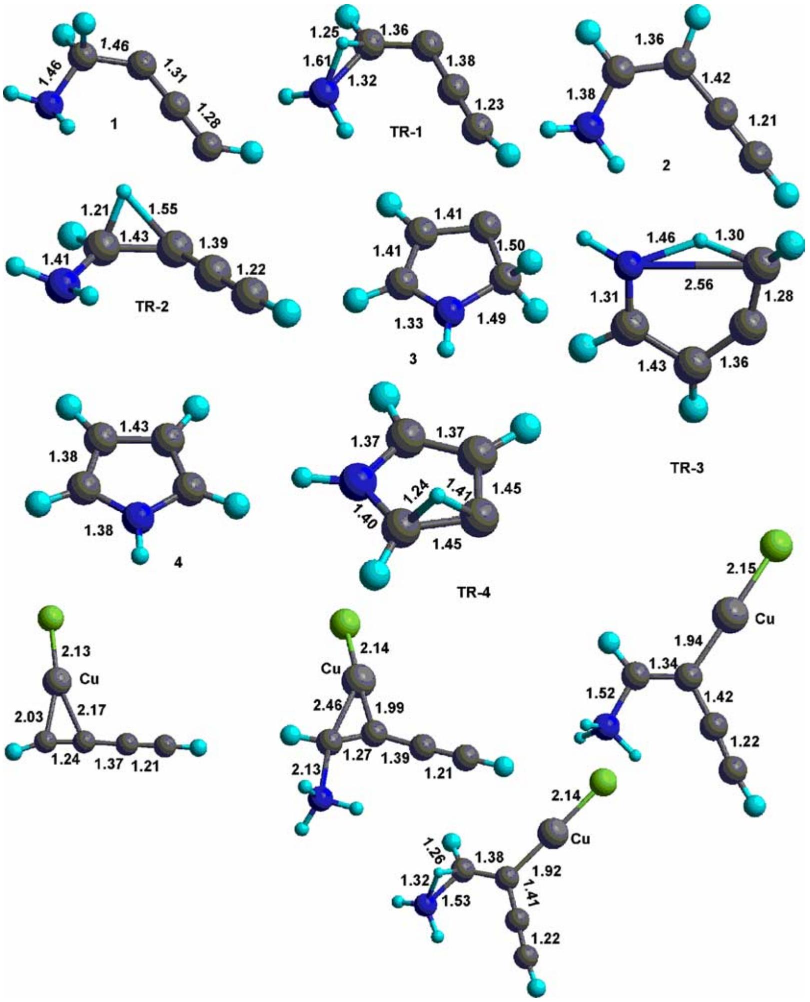


Fig. 1. B3LYP/6-31G* optimized geometries of reaction intermediates for catalyst-free reaction mechanism of pyrrole formation.