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Theoretical studies on the mechanism of oxazole with CO_2 catalyzed by gold(I) complexes

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ABSTRACT

The mechanism for the carboxylation reaction of oxazole with CO_2 catalyzed by N-heterocyclic carbene gold(I) complexes has been investigated using density functional theory calculation done at the B3LYP/6-31G(d, p) (SDD for Au) level of theory. The solvent effect was taken into account by B3LYP/6-311++G(d, p) (SDD for Au) single-point calculation with a polarizable continuum model (PCM) in THF. The calculations indicated that the reaction of (IPr)AuOH with oxazole proceeds through two competing pathways: five-centered transition state and four-centered transition state. The process of forming five-membered transition structure is more favored kinetically with a barrier of 31.7 kcal/mol versus 41.8 kcal/mol for the pathway of forming four-membered transition structure. The major pathway of the cycle involves the formation of a carbene intermediate. Subsequent step for reaction of this intermediate with CO_2 then provides the final carboxylate product. Meanwhile, the activation free energies for the different ligands or metal center also have been calculated and the same reactivity trends have been found. Our calculation results are good consistent with the experimental observation of Nolan and co-workers for N-heterocyclic carbene gold(I) complexes. The result predicts that (IPr)AgOH could be one of the highly chemical reactivity and stereoselective carboxylation reagent.

1. Introduction

Utilization of renewable resources is necessary for a sustainable society. Carbon dioxide, an abundant, inexpensive, nontoxic and biorenewable resource, has attracted increasing attention [1]. In the past decade, a great deal of research has been spent on activation and utilization of the thermodynamically and kinetically stable molecule with transition metal complexes [2–4]. As we know, the transition metal-catalyzed carboxylation reactions can occur by CO_2 with many unsaturated compounds [5–10]. Meanwhile, CO_2 activated by organometallic compounds has attracted theoretical studies interests for carboxylation reactions [11]. In this regard, it is widely accepted the reaction mechanism by Dang and Lin established that the reaction process produce the copper(I) alyl species and CO_2 insertion into the Cu—R bond of the intermediate. However, very recently, another possible pathway involves the formation of a carbene intermediate has been proposed by Ariafard using a theoretical study, and the carbene intermediate can isomerize to the experimentally observed structure of the catalytic cycle.

On the other hand, gold homogeneous catalysis has been the interesting subject of numerous theoretical studies due to its many applications in organic chemistry. Recently, Nolan and co-workers studied that aromatic heterocyclic carbene, such as oxazole, can be carboxylated by reaction with CO_2 in the presence of the catalyst (IPr)AuOH in THF at 45 °C [12], and subsequently produced oxazole 2-carboxylic acid by a quantitative yield (see Scheme 1). According to the experimental results, a plausible mechanism has been proposed to explain this novel gold(I)-catalyzed carboxylation. As depicted in Scheme 2, the proposed mechanism involves three steps.**1**. First, (IPr)AuOH and oxazole undergoes a metathesis of oxazolyl to form the gold(I) oxazolyl species **2**. Following, insertion of CO_2 into the Au—C bond of **2** through nucleophilic attack gives the carboxylate complex **3**. Finally, a ligand exchange with —OH followed by hydrolysis gives the final carboxylated product [12]. Recently, a new mechanism including the formation of a carbene intermediate for copper catalyst has been proposed by Ariafard using a theoretical study. It is interesting to note whether the reaction takes place by the proposed mechanism or the other possible mechanism involving a carbene intermediate.

To the best of our knowledge, there are no detailed theoretical studies available for this novel gold(I)-catalyzed carboxylation reported by Nolan and co-workers [12]. In this paper, for the sake of a more thorough discussion and explanation the experiment

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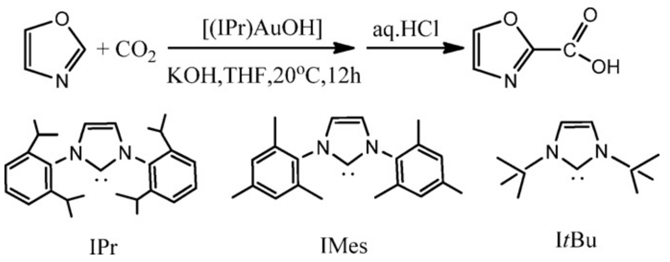
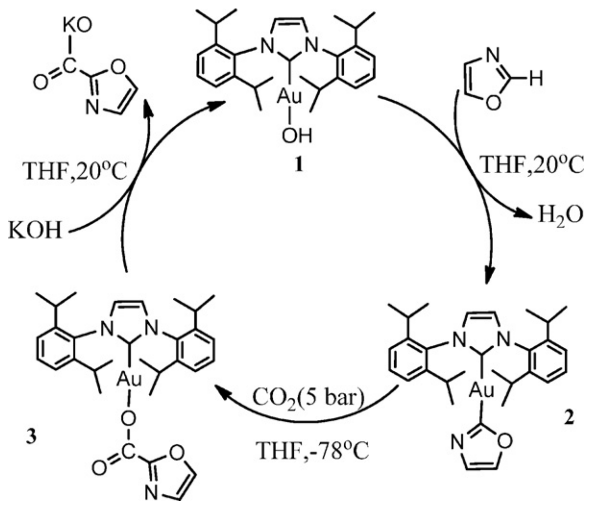


Scheme 1. Carboxylation of oxazole with NHC-gold(I) catalysts.

result, we present a detailed density functional theory (DFT) computational investigation for the mechanism of the gold(I)-catalyzed synthesis of highly substituted oxazole based on the experimental evidence reported by Nolan and co-workers [12]. From the results shown here, we attempt to gain a more detailed understanding of the catalytic mechanism. Meanwhile, we expect to find out more about the factors that control the activation barriers of this important reaction and further investigate the effects of solvent on the thermodynamic and kinetic properties of these reactions. This paper also discusses how the different ligands and the different substrates on the potential energy surface affect the reaction activities. In addition, the DFT calculations are employed to compare and predict the reaction mechanisms and catalytic activities between (IPr)CuOH and (IPr)AgOH with oxazole, respectively. An understanding of the reaction mechanism will be helpful in the design of new catalyst for carboxylation of C—H bonds.

2. Computational details

The theoretical calculations were performed using the Gaussian 03 program [13], and all of the molecular geometries of the model complexes were fully optimized using density functional theory (DFT) method at the B3LYP level of theory [14]. The 6-31G basis set [15] with polarization (d) and (p) were used for all of the other atoms except gold, silver and copper, for which the Stuttgart–Dresden effective core potential [16] was employed to accurately account for relativistic effects and to substantially reduce the number of electrons in the system. Analytical frequency calculations at the same level have also been done to confirm all of the stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency) as well as to obtain the zero-point energy correction. The relative energies were thus corrected for the vibrational zero-point energies (ZPE, not scaled). The thermodynamic functions, including free energies, were calculated at 298.15 K and 1 atm. Furthermore, intrinsic reaction coordinate (IRC) calculations [17] were also carried out to verify that transition structures calculated indeed connect relevant reactants, products, and/or intermediates. In consideration of the solvent effects on the reactions of interest, we applied a continuum medium to do single-point salvation energy calculations for all of the species calculated along the minimum energy pathway, using UAHF radii on the polarizable continuum model (PCM) [18–20]. The PCM calculations were done at the B3LYP/PCM/6-311++G(d, p)//B3LYP/6-31G(d, p) (SDD for Au, Ag and Cu) level of theory. THF was used as the solvent, corresponding to the experimental conditions, and the dielectric constant was assumed to be 7.58 for bulk THF solvent.



Scheme 2. Plausible mechanism were proposed for carboxylation of oxazole using (IPr)AuOH by Nolan and co-workers.

3. Results and discussions

Free energy profiles for the different reaction pathways of the catalytic cycles [21] are shown in Figs. 1 and 2. The optimized stationary structures (minima and saddle points) on the potential energy surfaces of the reactions are depicted schematically in Figs. 3 and 4 with selected key geometry parameters (bond lengths). The relative energies, activation energies, the relative free energies and activation free energies in gas phase and in solution are listed in Tables 1 and 2. Unless otherwise noted, the relative energies and the relative free energies discussed in subsequent sections refer to the value in THF solvent. The detailed structural parameters and energies for the structures determined here are collected in the Supporting Information. In order to keep the computational cost low, the original (IPr)AuOH was selected with ligand IPr replaced with 1,3-biphenyl-imidazol-2-ylidene as a model.

3.1. Carboxylation of oxazole with CO_2 using (IPr)AuOH catalysts

Free energy profile for this process is represented in Fig. 1. The structures of the various critical points located on the potential surface along with the values of the most relevant geometry parameters are shown in Fig. 3. From the energy profile, it is evident that the first step involves a precursor complex **PC1**, where the 2-hydrogen atom of oxazole interacts with the oxygen atom of (IPr)AuOH. The preliminary complex **PC1** is 6.1 kcal/mol less stable than the reactants **R1** + **a** (oxazole) shows a slight C—H activation. From **PC1**, two different pathways for C—H activation were located. One pathway involves the five-membered transition structure **TS1a** in which the nitrogen atom of the heterocycle interact with the Au metal center. Meanwhile, the proton is being transferred from the heterocycle to the hydroxyl oxygen atom. **TS1a** has only one imaginary frequency of 257.6i cm^{-1}, and IRC calculations confirmed that this TSs connects the corresponding precursor complex and the intermediates. Another pathway takes place through the four-centered transition structure **TS2a**, which corresponds to the migration of the oxazolyl fragment to the Au atom concomitant with the proton transfer from oxazole to the OH ligand. Vibrational analysis shows that the **TS2a** structure have one imaginary frequency of 499.7i cm^{-1} and was confirmed to be the first-order saddle point. Both processes produce intermediates **1a** and **2a** respectively and release one H_2O. As shown in Fig. 3, the Au—N, Au—O^1, O^1—H^2, C^1—H^2 bond lengths are 2.123 Å, 2.651 Å, 1.487 Å and 1.189 Å respectively in **TS1a**, and the Au—O^1 and Au—C(IPr) bond lengths elongated by 0.640 Å (2.011 Å in **PC1**) and 0.008 Å (2.000 Å in **PC1**) respectively upon going from the preliminary complex to the transition state. In **TS2a**, the oxygen atom is completely connected with the H^2 of the oxazole (the bond distance O^1—H^2 is 1.104 Å). Meanwhile, the bonds of the Au—O^1 and