

Alkylselenite-catalyzed Oxidative Carbonylation of Amines: Density Functional Theory Study

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Ureas and carbamates have been conventionally produced by the reaction of amines with phosgene. However, phosgenation processes raise severe environmental concerns, which are attributed to the toxicity of phosgene and the formation of corrosive hydrogen chloride as a co-product. The considerable industrial interest in replacing current phosgene-based processes prompted several methods using non-phosgene routes including carbonylation of amines or nitro compounds and carbomethoxylation of amines with dialkylcarbonates.¹ Among these, catalytic oxidative carbonylation of an amine in the presence of alcohol has been studied most extensively.² Catalytic systems based on precious metals such as Rh and Pd are commonly used for this purpose, but most of these catalytic systems suffer from either low reactivity or severe reaction conditions such as high temperature and pressures.³ Alkali metal selenites and imidazolium alkylselenites have also been successfully employed by our group for the oxidative carbonylation of aromatic amines to produce diarylurea and/or arylcarbamates (Eq. 1).⁴



However, the relative difficulty of obtaining mechanistic information about reactions that only proceed under conditions of elevated temperature and pressures prevented us from extensively studying reaction pathways. In the previously proposed mechanism for the reaction, CO is assumed to be inserted between selenium-nitrogen bond in an important step (Eq. 2).^{4d}



Since we have studied CO insertion between metal-alkyl bond using density functional theory (DFT) method before,⁵ we tried to apply the same approach to Se-N bond to see whether the above assumption holds theoretically. However, DFT calculation shows that CO cannot be inserted into that bond probably because Se is semimetal with high-lying *d* orbitals, but CO rather acts as a reducing agent in this reaction to reduce Se(IV) to Se(II). This finding and the evidence of the formation of CO₂ under the experimental conditions as shown in Figure 1 have prompted us to investigate the whole catalytic cycle in more detail using theoretical method.

In the present communication, we describe the catalytic cycle for the oxidative carbonylation of an amine in the presence of a methylselenite catalyst using DFT method.

DFT calculation was performed using Gaussian 09 program.⁶ Methyl amine was chosen as the model amine since it is the simplest system to resemble our catalytic reactions. Only anion part of the catalyst was taken into account since cation part does not affect the reaction mechanism even though it might change the energy barrier a little. The geometry optimizations and thermodynamic corrections were performed with hybrid Becke 3-Lee-Yang-Parr (B3LYP) exchange-correlation functional with the 6-31+G* basis sets

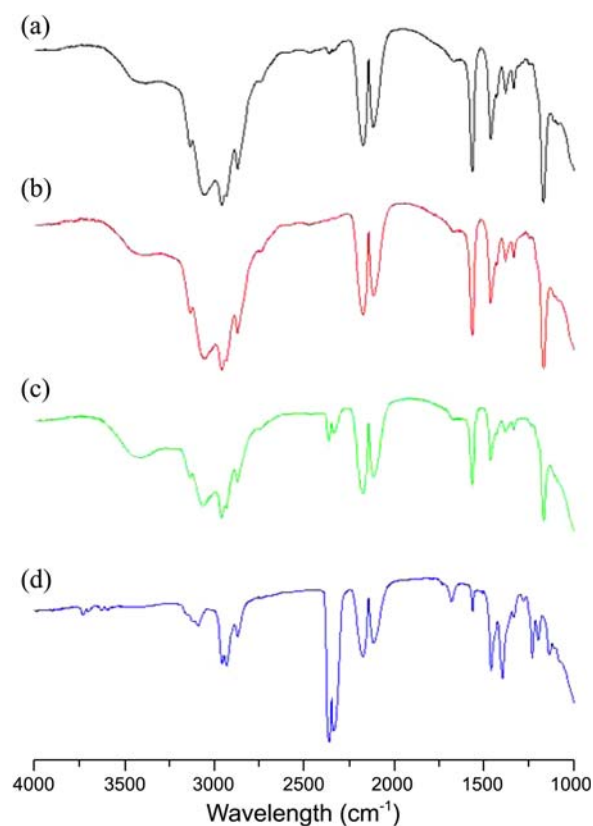


Figure 1. IR spectra showing the formation of CO₂ under experimental conditions for the oxidative carbonylation of amine catalyzed by methylselenite. (a) 60 °C, (b) 80 °C, (c) 100 °C, and (d) after 4 h at 100 °C.

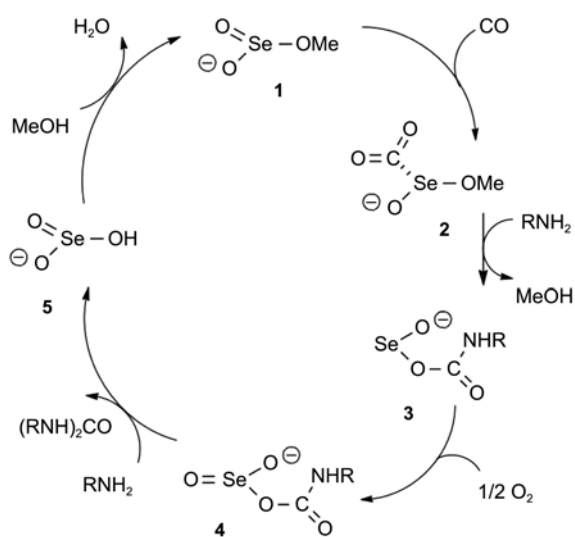


Figure 2. Catalytic cycle for the oxidative carbonylation of amine catalyzed by methylselenite.

for C, H, N, and O and LanL2DZ (ECP) basis sets for Se. All stationary points were verified as minima by full calculation of the Hessian and a harmonic frequency analysis.

As mentioned previously, no insertion reaction surface could be found theoretically for the interaction between $[\text{Se}^{\text{IV}}\text{O}_2(\text{NHCH}_3)]^-$ and CO and instead $[\text{Se}^{\text{IV}}\text{O}_2(\text{NHCH}_3)]^-$ would take up one molecule of CO to be reduced to $[(\text{CO}_2)\text{Se}^{\text{II}}\text{O}(\text{NHCH}_3)]^-$. Therefore, amine has to come from second coordination sphere to attack CO_2 and to produce urea as shown in Figure 2. Optimized structures of reaction intermediates and transition states involved in the oxidative carbonylation of amine catalyzed by methylselenite are shown in Figure 3.

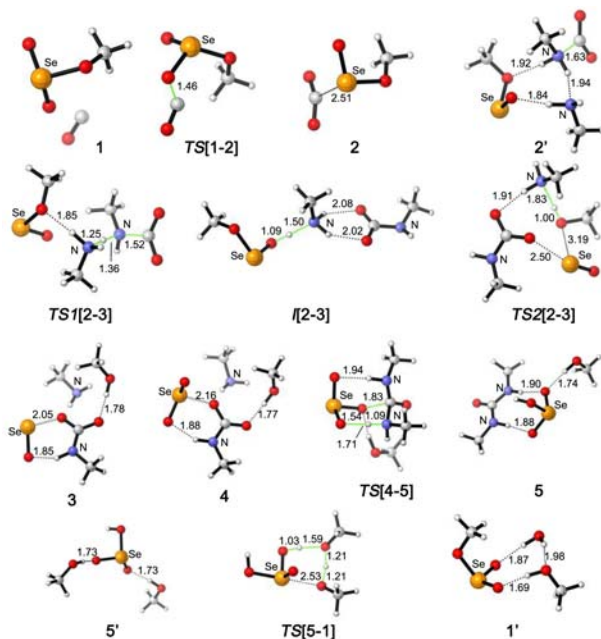


Figure 3. Optimized structures of reaction intermediates and transition states involved in the oxidative carbonylation of amine catalyzed by methylselenite.

Accordingly, in the first step of catalytic cycle, the solvated anionic catalyst $[\text{Se}^{\text{IV}}\text{O}_2(\text{OCH}_3)]^-$ (**1**) is reduced by CO to produce CO_2 and methylhyposelenite $[\text{Se}^{\text{II}}\text{O}(\text{OCH}_3)]^-$ (**2**). The free energy of activation (ΔG^\ddagger) is 35.5 kcal/mol for $\text{TS}[1-2]$ and the free energy of reaction (ΔG) is -34.1 kcal/mol. The hyposelenite anion can hold onto CO_2 until amine arrives to react. The enthalpy for the interaction between CO_2 and the hyposelenite anion is calculated to be -4.8 kcal/mol. This CO_2 is immediately captured by amine to produce intermediate ammonium carbamate (**I[2-3]**) in the second step, since it is well known that primary amine is very reactive in capturing CO_2 .⁷ At the same time ammonium ion protonates anionic methylhyposelenite releasing methanol and letting carbamate coordinate to selenium (**3**). The free energies of activation (ΔG^\ddagger) are 8.6 kcal/mol and 22.1 kcal/mol for the capturing CO_2 ($\text{TSI}[2-3]$) and the releasing methanol ($\text{TS2}[2-3]$) step, respectively. And the free energies of reaction (ΔG) are -13.5 kcal/mol and -5.0 kcal/mol for the capturing and the releasing step, respectively.

In the third step, Se^{II} is reoxidized to Se^{IV} (**4**) to make it easier for amine to attack carbonyl group, since Se in higher oxidation state can pull the electron density more from carbonyl carbon in the transition state. The activation energy for this step is not calculated since paramagnetic oxygen is involved and usually oxidation step is not rate-determining. The free energy of reaction (ΔG) for this step is -24.8 kcal/mol. In the fourth step, amine attacks the carbonyl carbon to produce urea (**5**). Previously this step is assumed to proceed *via* tetrahedral intermediate. But O-C bond in $^-\text{O}_2\text{SeOCONHR}$ becomes very weak with 1.83 Å in the transition state because of high oxidation state of Se, and so the reaction proceeds without going through tetrahedral intermediate. This intermediate-free pathway is more favorable by 8.6 kcal/mol than the tetrahedral-intermediate pathway. The free energy of activation (ΔG^\ddagger) for the urea formation is 41.4 kcal/mol for $\text{TS}[4-5]$ and the free energy of reaction (ΔG) is -8.8 kcal/mol. The final step is to regenerate the methylselenite catalyst (**1**). This step proceeds through four-coordinate transition state. Because of the lone pair present in the

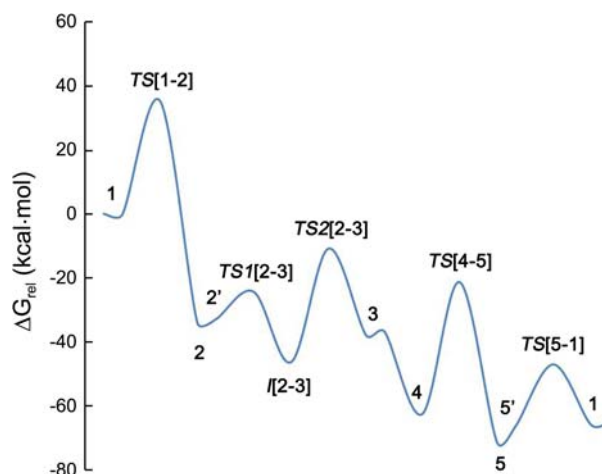


Figure 4. Calculated free energy profile for the oxidative carbonylation of amine catalyzed by methylselenite.

selenium, this four coordinate species takes the see-saw shape with lone pair on the equatorial position of the trigonal bipyramidal structure. The free energy of activation (ΔG^\ddagger) for the regeneration of the catalyst is 19.3 kcal/mol for **TS[5-1]** and the free energy of reaction (ΔG) is 0.5 kcal/mol.

The complete free energy profile for the oxidative carbonylation of amine catalyzed by methylselenite is shown in Figure 4. As shown, the rate determining step is the reduction step of Se(IV) by CO to Se(II) producing CO₂ and the total free energy of reaction to produce urea and water from two molecules of amine and CO is -65.9 kcal/mol.

In conclusion, the facile change of selenium oxidation state by CO and O₂ might be the main reason for the activity of the selenium catalyst for this reaction.

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