A Theoretical Study on the Generation Process of Carbonyl Selenide in Selenium Catalyzed Carbonylation of Amines

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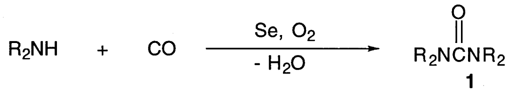
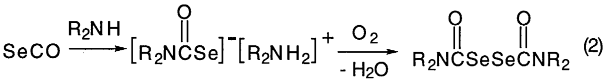
Ab initio molecular orbital calculations were performed in order to examine the regeneration pathways of carbonyl selenide which plays an important role in selenium catalyzed carbonylation of amines with carbon monoxide.

We have already revealed that selenium has a very unique catalytic activity for carbonylation of amines with carbon monoxide (eq. 1).[1] This reaction proceeds at room temperature under 1 atom of carbon monoxide in the presence of oxygen to give corresponding ureas (**1**) quantitatively.



$$\mathrm{R_2NH} + \mathrm{CO} \xrightarrow[\text{- H}_2\text{O}]{\text{Se, O}_2} \underset{\mathbf{1}}{\mathrm{R_2N\overset{O}{\overset{\|}{C}}NR_2}} \tag{1}$$

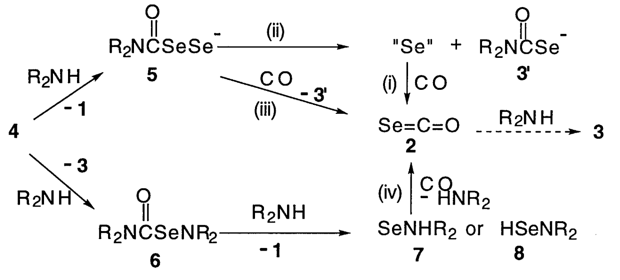


$$\underset{\mathbf{2}}{\mathrm{SeCO}} \xrightarrow{\mathrm{R_2NH}} \underset{\mathbf{3}}{[\mathrm{R_2N\overset{O}{\overset{\|}{C}}Se}]^-[\mathrm{R_2NH_2}]^+} \xrightarrow[\substack{\text{- H}_2\text{O}\\ \text{- R}_2\text{NH}}]{\mathrm{O_2}} \underset{\mathbf{4}}{\mathrm{R_2N\overset{O}{\overset{\|}{C}}SeSe\overset{O}{\overset{\|}{C}}NR_2}} \tag{2}$$

As for the reaction pathways of selenium catalyzed carbonylation of secondary amines, it has been confirmed experimentally that the reaction involves (a) addition of amines to carbonyl selenide (**2**) yielding carbamoselenoates (**3**),[2] and (b) successive oxidation of **3** with oxygen to afford biscarbamoyl diselenides (**4**) (eq. 2).[3] Although it was also revealed that treatment of **4** with amines gives corresponding ureas (**1**) accompanied by regeneration of **3** and selenium,[3] the pathway for regeneration of **2** is still in question. In order to shed light on this process, with which the catalytic cycle is completed, three plausible pathways for generation of **2** from **4** were examined by means of *ab initio* molecular orbital calculations.

Calculations were performed at the RHF and/or RMP2 levels of theories using Gaussian 92.[4] As the basis set for selenium, a relativistic effective core potential with a double-zeta basis set[5] augmented with polarization *d*-orbitals (ζ = 0.338)[6] and diffuse *sp*-orbitals (ζ = 0.037)[7] was used unless otherwise stated. Basis sets specified in this paper, such as 3-21+G, 6-31+G*, and 6-311+G*, refer only to those adopted for hydrogen and first-raw elements. Five component orbitals were used for *d*-functions.

Plausible pathways for regeneration of **2** from **4** are illustrated in Scheme 1. Diselenide **4** can react with an amine molecule at two sites, i.e., at the carbonyl carbon or at a selenium leading to **5** or **6**, respectively. The former carries an ammonium counter ion which was omitted in Scheme 1. The latter may undergo aminolysis to form urea (**1**) along with **7** or **8**. Theoretical calculations were performed with respect to the following 4 steps (i-iv) leading to carbonyl selenide from the intermediates **5**, **7**, and **9**. Figure 1 shows structures and selected geometrical parameters of intermediates, complexes,[8] and transition states optimized at the HF/3-21+G level. All these stationary structures were checked by vibrational frequency calculations to have C_s symmetries except **2** which is linear.



Scheme 1. Ring closing pathways of the catalytic cycle for selenium catalyzed carbonylation of secondary amines with carbon monoxide.

Reaction of atomic selenium with carbon monoxide leading to **2** (step i) was found to be largely exothermic. The energy changes, $\Delta E_{(i)}$, calculated at various levels were listed in Table 1, which indicates that the values largely vary depending on the levels of theories but are much less sensitive to the basis sets. Step ii, which corresponds to liberation of atomic selenium from **5**, was calculated with R = H, and the energy change, $\Delta E_{(ii)}$, was listed in Table 1. This process is largely endothermic, so this pathway (steps i + ii) is not likely to operate under mild conditions as in the case of present selenium catalyzed carbonylation systems. But these results do not contradict an evidence that selenium reacts directly with carbon monoxide at high temperatures (> 500 °C).[9]

Table 1. Energy changes of steps i-iv in kcal/mol

level of calculations	step i	step ii	step iii[a]				step iv[b]			
	$\Delta E_{(i)}$	$\Delta E_{(ii)}$	**9**	**10**	**11**	**2 + 3'**	**12**	**13**	**14**	**2** + Me_2NH
HF/3-21+G//HF/3-21+G	-60.1	65.1	-2.2	11.8	-1.7	5.0	-1.4	1.4	-10.2	-5.0
HF/6-311+G*[c]//HF/3-21+G	-58.7						-0.1	4.9(4.8)	-10.5	-8.3(-10.3)
MP2/3-21+G//HF/3-21+G	-86.8	82.5	-2.4	4.0	-13.9	-4.3	-2.8	-4.0	-22.8	-15.6
MP2/6-31+G*//HF/3-21+G	-88.6	83.1	-2.0	6.3	-14.2	-5.5	-2.0	-2.1	-25.5	-19.8
MP2/6-311+G*[c]//HF/3-21+G	-89.9	83.6	-1.7	6.1	-14.9	-6.3	-1.7	-2.2(-2.9)	-26.3	-20.8(-22.3)
MP2/6-311+G*//HF/6-31+G*	-89.2						-1.4	-1.3	-25.8	-20.9
MP2/3-21+G//MP2/3-21+G	-87.8						-3.1	-3.1	-23.9	-16.6
MP2/6-311+G*//MP2/3-21+G	-90.9						-1.6	-1.3	-27.7	-22.4
MP2/6-311+G*//MP2/6-311+G*	-90.4									

[a] Relative to the total energy of **5** + CO. [b] Relative to the total energy of **7** + CO. [c] Numbers in parentheses are relative energies calculated using split Huzinaga's 43321/4321/4 basis set for selenium[6] with the same polarization and diffuse functions.

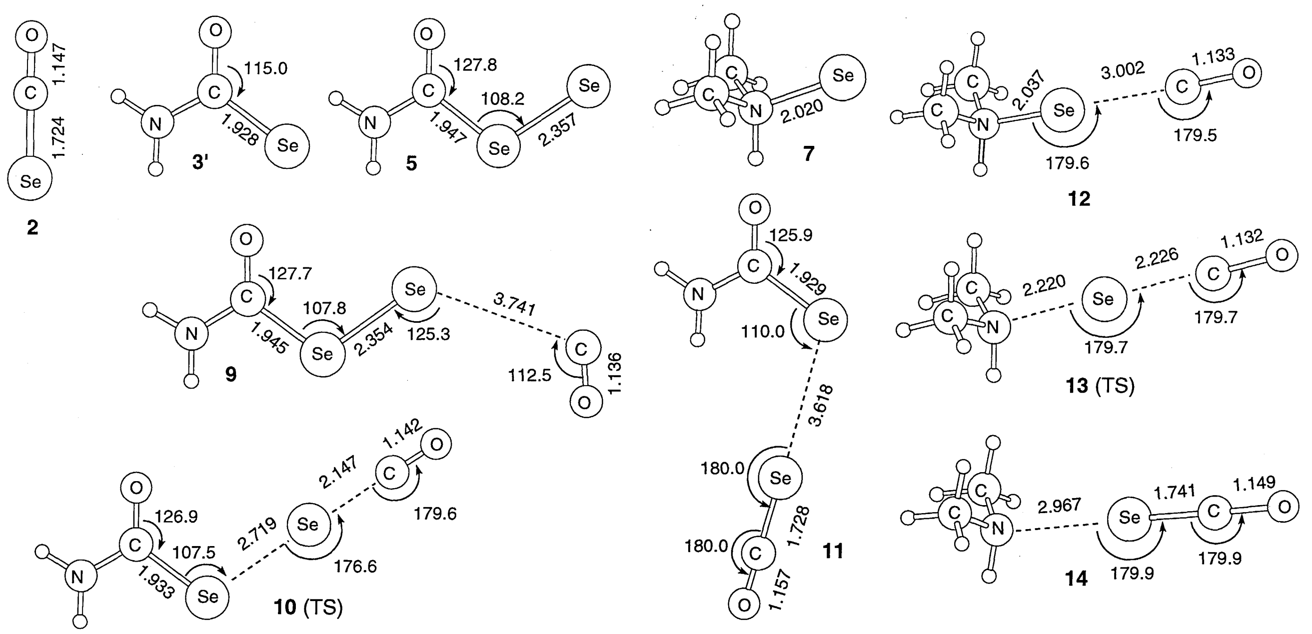


Figure 1. Optimized structures at the HF/3-21+G level. Distances and angles are in Å and degrees, respectively.

For both steps, energies change monotonically along the reaction coordinates and no transition states or complexes were found.

Step iii is a direct reaction of **5** with carbon monoxide without elimination of selenium giving rise to **2** and **3'**. Calculation of this process with R = H afforded a transition state (**10**) which has a linear structure with respect to the Se-Se-C-O bonds. Energy changes along the reaction coordinate relative to the total energy of **5** and CO were summarized in Table 1. The small $\Delta E^{\ddagger}$ of 6.1 kcal/mol indicates that this process is quite reasonable in comparison to the pathway via steps i and ii.

Prior to the calculation of step iv, we compared stabilities of amine selenide **7** and aminoselenol **8**, since aminolysis of **6** can give either compounds. Calculations with R = Me at the MP2/6-311+G*//HF/3-21+G level revealed that **7** is more stable than *anti*-**8** by 5.8 kcal/mol,[10] indicating that **7** is the more suitable intermediate. So we calculated the reaction of **7** with CO at various levels. Relative energies of the transition state (**13**), complexes (**12**, **14**), and resulting compounds (**2** + Me_2NH) of this step are shown in Table 1. It is very interesting that this process is energetically downhill or has an early transition state, if present, with a very small activation energy. Use of an all electron basis set for selenium did not cause any significant change in calculated energies at both HF and MP2 levels.

In conclusion, a pathway via steps i and ii can be ruled out since elimination of atomic selenium is energetically very unfavorable. Pathways via step iii or iv are both likely, but the latter may be favored if **7** can be generated at an appreciable rate in the reaction media.

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7 . The ζ value was determined so as to afford the lowest energy for Me_2NSe^- at the Hartree-Fock level using the 3-21+G basis set for H, C, and N atoms.

8 Several other complexes were found but only meaningful ones for the present study were shown.

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10 The *anti*-**8**, which has a hydrogen *anti* to the lone pair on the nitrogen, is more stable than its *syn* isomer by 2.9 kcal/mol.