

PRIORITY COMMUNICATION

The Role of Alkali Metal Carbonate on the SeO₂-Catalyzed Oxidative Carbonylation of Cyclohexylamine and Aniline

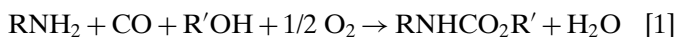
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There have been numerous attempts to produce carbamates by using nonphosgene methods (1–6). One of the approaches is the catalytic oxidative carbonylation of an amine in the presence of carbon monoxide, oxygen, and alcohol using catalyst systems containing group VIII transition metals or their compounds (2, 6–8). The use of selenium metal or compounds of selenium has also been reported for the production of aliphatic and alicyclic carbamates (9, 10). However, in the case of oxidative carbonylation of aromatic amine, the yields of carbamates are extremely low even with the use of large quantities of catalyst, selenium, or compounds of selenium.

We now report that a catalyst system comprising SeO₂ and alkali metal carbonate is very effective for the production of cyclohexyl carbamate and phenyl carbamate directly from cyclohexylamine and aniline, respectively as illustrated in Eq. [1],



(R = cyclohexyl or phenyl, R' = methyl or ethyl).

A 100-ml stainless steel Parr reactor with a magnetic drive stirrer and an electrical heater was charged with cyclohexylamine or aniline, methanol, SeO₂, alkali metal carbonate if necessary, and toluene as an internal standard. The reactor was purged with nitrogen followed with CO and then pressurized to about 4.08 MPa with a gas mixture of O₂ and CO (molar ratio of O₂/CO = 20/80). The bomb was then heated with agitation to a specified reaction temperature (120 or 160°C) with the addition of O₂/CO mixture gas from a reservoir tank (ballast tank) up to 6.80 MPa of O₂/CO pressure. After the reaction, the bomb was cooled to room temperature, vented, and the product mixture removed. The product mixture was analyzed by GC, GC-Mass, and HPLC. The catalyst mixture was characterized by elemental analysis, XRD, and NMR.

The results of the SeO₂-catalyzed oxidative carbonylations of cyclohexylamine and aniline performed with or without the presence of alkali metal carbonate are shown in Tables 1 and 2. Both cyclohexylamine and aniline were carbonylated in the presence of SeO₂, as well as alkali metal carbonate to give the corresponding ureas and/or carbamates. However, no carbonylation of aniline was observed in the absence of alkali metal carbonate. The conversion of cyclohexylamine was almost quantitative under the experimental conditions, irrespective of the presence of alkali metal carbonate. The presence of the carbonate increased the yield of cyclohexyl carbamate up to 1.6 times, depending on the carbonate used. The higher yield of carbamate by the presence of alkali metal carbonate can be rationalized by the fact that alkali metal carbonate itself is able to catalyze the transformation of intermediate, dicyclohexyl or diphenyl urea, into the corresponding carbamate as shown in Table 3. The activity of the SeO₂-alkali metal carbonate catalyst system for the carbonylation of aniline was found in the order SeO₂-Cs₂CO₃ ≅ SeO₂-Rb₂CO₃ > SeO₂-K₂CO₃ > SeO₂-Na₂CO₃ > SeO₂-Li₂CO₃, suggesting that the size and ionization tendency of the alkali metal ion and the solubility of alkali metal carbonate might play an important role.

In order to have a better understanding of the role of alkali metal carbonate, various experiments were carried out. Potassium carbonate (5 mmol) and SeO₂ (10 mmol) were reacted in methanol (25 ml) at room temperature for 1 h. As soon as the carbonate was added to the methanolic solution of SeO₂, CO₂ started to evolve. The resulting solution was dried in a glove box under vacuum to give a white solid. The same compound was also obtained from the reaction of SeO₂ with potassium carbonate conducted in methanol for 2 h at 120°C under 6.80 MPa of O₂/CO (O₂/CO = 20/80). Even though the compound is not fully identified yet by X-ray crystallography, due to the difficulty in obtaining single crystals, the compound is believed to be KSeO₂(OCH₃) as in Eq. [3] from the elemental analysis

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TABLE 1

 Effect of Alkali Metal Carbonates on the Oxidative Carbonylation of Cyclohexyl Amine^a

Catalyst	M ₂ CO ₃	Conv. (%)	Selectivity (%)	
			Carbamate ^b	Urea ^c
SeO ₂	None	99.6	25.5	73.8
SeO ₂ ^d	None	100	98.3	tr.
None	K ₂ CO ₃	94.0	—	(98.9) ^e
SeO ₂	Li ₂ CO ₃	99.8	26.2	71.8
SeO ₂	Na ₂ CO ₃	99.8	30.2	69.3
SeO ₂	K ₂ CO ₃	99.7	34.7	65.1
SeO ₂	Rb ₂ CO ₃	99.9	39.2	57.4
SeO ₂	Cs ₂ CO ₃	99.9	41.5	47.6

^a Condition: cyclohexylamine 10 mmol, catalyst 0.2 mmol, M₂CO₃ = 1 mmol, toluene 1 g (internal standard), methanol 25 ml, temperature 120°C, pressure 6.80 MPa (O₂/CO = 20/80), reaction time 1 h.

^b Carbamate = methyl-N-cyclohexyl carbamate.

^c Urea = N,N'-dicyclohexyl urea.

^d Reaction temp. = 160°C.

^e N-cyclohexylformamide.

[calculated: Se (43.6%), K (21.5%), C (6.6%), H (1.7%); found: Se (42.7%), K (21.4%), C (6.8%), H (1.8%)], ¹H NMR [CD₃OD, δ 3.35 (s)] and ¹³C NMR [CD₃OD, δ 50.15] results. Interestingly, it was observed that KSeO₂(OCH₃) was slowly transformed into a new crystalline compound upon exposure (Eq. [4]). As shown in Fig. 1, the XRD pattern of the new compound is in good agreement with that of K₂Se₂O₅ listed in JCPDS handbook and this is also supported by the elemental analysis result [calculated: Se (50.0%), K (24.7%); found: Se (48.8%), K (24.5%)].

SeO₂ reacts with methanol first to give (MeO)Se(=O)(OH) which was characterized by elemental analysis [calcu-

TABLE 2

 Effect of Alkali Metal Carbonates on the Oxidative Carbonylation of Aniline^a

Catalyst	M ₂ CO ₃	Conv. (%)	Selectivity (%)	
			Carbamate ^b	Urea ^c
SeO ₂	None	N.R.		
None	K ₂ CO ₃	N.R.		
SeO ₂	Li ₂ CO ₃	60.1	40.4	57.6
SeO ₂	Na ₂ CO ₃	61.4	52.1	45.8
SeO ₂	K ₂ CO ₃	76.4	82.7	14.9
SeO ₂	Rb ₂ CO ₃	80.8	93.4	5.5
SeO ₂	Cs ₂ CO ₃	81.6	92.0	6.4
K ₂ Se ₂ O ₅	None	56.2	75.8	22.1
KSeO ₂ (OCH ₃)	None	57.0	78.5	19.3

^a Condition: aniline 10 mmol, catalyst 0.2 mmol, M₂CO₃ = 1 mmol, toluene 1 g (internal standard), methanol 25 ml, temperature 120°C, pressure 6.80 MPa (O₂/CO = 20/80), reaction time 2 h.

^b Carbamate = methyl-N-phenyl carbamate.

^c Urea = N,N'-diphenyl urea.

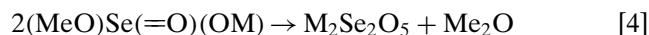
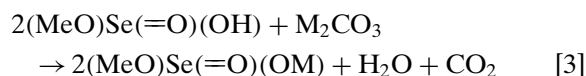
TABLE 3

 Effect of Alkali Metal Carbonates on the Formation of Carbamate from Urea and Methanol^a

Urea	M ₂ CO ₃	Conv. (%)	Selectivity (%)
Dicyclohexyl urea	Li ₂ CO ₃	69.4	97.7
Dicyclohexyl urea	Na ₂ CO ₃	70.8	98.3
Dicyclohexyl urea	K ₂ CO ₃	93.6	98.1
Dicyclohexyl urea	Rb ₂ CO ₃	95.4	97.8
Dicyclohexyl urea	Cs ₂ CO ₃	98.2	97.9
Diphenyl urea	Li ₂ CO ₃	81.6	98.3
Diphenyl urea	Na ₂ CO ₃	87.4	97.9
Diphenyl urea	K ₂ CO ₃	91.3	98.2
Diphenyl urea	Rb ₂ CO ₃	93.1	97.7
Diphenyl urea	Cs ₂ CO ₃	95.2	98.4

^a Condition: urea 10 mmol, M₂CO₃ 1 mmol, methanol 25 ml, temperature 160°C, reaction time 2 h.

lated: Se (55.2%), C (8.4%), H (2.8%); found: Se (54.7%), C (8.2), H (2.8)], and ¹H NMR [CD₃OD, δ 3.35 (s)], and the subsequent reaction of (MeO)Se(=O)(OH) with M₂CO₃ would produce M₂Se₂O₅ as in Eqs. [3], [4]:



The catalytic activities of KSeO₂(OCH₃) and K₂Se₂O₅ were almost comparable to those obtained from the reaction

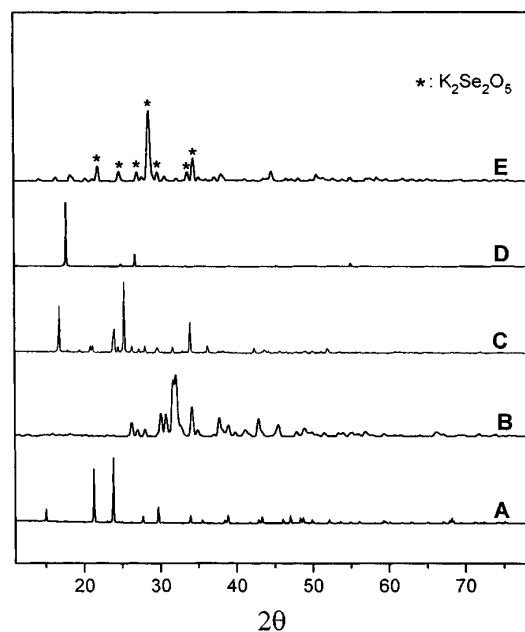


FIG. 1. XRD patterns of A–E: A. SeO₂; B. K₂CO₃; C. SeO(OCH₃)(OH); D. KSeO₂(OCH₃); E. After exposing the sample D to air.

performed the presence of SeO_2 and K_2CO_3 (Table 2), implying that $\text{MSeO}_2(\text{OCH}_3)$ and $\text{M}_2\text{Se}_2\text{O}_5$ may act as active species. It is surprising that, unlike SeO_2 , alkali metal containing selenium compounds, $\text{MSeO}_2(\text{OCH}_3)$ or $\text{M}_2\text{Se}_2\text{O}_5$, show activities in the aniline carbonylation reaction. It is generally accepted that the carbonylation of an amine by a platinum group metal proceeds via the following steps: coordination of the amine to the metal center through the nitrogen atom, N–H bond dissociation (M–H bond formation), and CO insertion into the metal–nitrogen bond. However, in the carbonylation of an amine catalyzed by SeO_2 , $\text{MSeO}_2(\text{OCH}_3)$ or $\text{M}_2\text{Se}_2\text{O}_5$, interaction of the amino group ($-\text{NH}_2$) with $[\text{Se}=\text{O}]$ forming a $[\text{Se}-\text{OH}]$ bond seems to be involved in the first stage of the reaction, in addition to the coordination to Se through the nitrogen atom. The catalytic activity of a selenium compound containing a $[\text{Se}=\text{O}]$ bond is therefore strongly dependent on the ability of abstracting a H atom from the $-\text{NH}_2$ of the amine. The oxygen atom of $[\text{Se}=\text{O}]$ in $\text{SeO}_2(\text{OCH}_3)^-$ or $\text{Se}_2\text{O}_5^{2-}$ is obviously more basic than that in SeO_2 , that is, more powerful in abstracting a H atom from the amino group. This is probably the reason for the activities of $\text{MSeO}_2(\text{OCH}_3)$ and $\text{M}_2\text{Se}_2\text{O}_5$ in the carbonylation of aniline which is regarded as a much weaker base than cyclohexylamine.

The carbonylation reaction was sensitive to the amount of alkali metal carbonate added. Table 4 shows that the conversion and the yield of carbamate increase with increasing amount of K_2CO_3 . This indicates that, in addition to making an active selenium species, the alkali metal carbonate also plays a role in promoting the CO insertion into the metal–nitrogen bond by providing a basic environment as in the industrial production of N,N'-dimethylformamide from the NaOCH_3 -catalyzed carbonylation of N,N'-dimethylamine (11). In fact, the reaction of cyclohexylamine with CO in the presence of K_2CO_3 produced N-cyclohexylformamide in high yield over 90% (Table 1).

Efforts to fully characterize the active species and to elucidate the mechanism of the present reaction catalyzed by SeO_2 and alkali metal carbonate are now under progress,

TABLE 4
Effect of Molar Ratio of $\text{SeO}_2/\text{K}_2\text{CO}_3$ on the Oxidative Carbonylation of Cyclohexylamine and Aniline^a

Amine	$\text{SeO}_2/\text{K}_2\text{CO}_3$	Conv. (%)	Selectivity (%)	
			Carbamate ^b	Urea ^c
Cyclohexylamine	1/1	99.7	28.2	70.3
Cyclohexylamine	1/2	99.4	29.4	69.6
Cyclohexylamine	1/5	99.7	34.7	65.1
Cyclohexylamine	1/10	99.9	43.0	56.0
Aniline	2/1	59.0	67.6	29.8
Aniline	1/1	68.9	62.8	35.6
Aniline	1/2	76.3	65.5	32.4
Aniline	1/5	76.4	82.7	14.9
Aniline	1/10	74.3	94.2	3.7

^a Condition: amine 10 mmol, SeO_2 0.2 mmol, toluene 1 g (internal standard), methanol 25 ml, temperature 120°C, pressure 6.80 MPa ($\text{O}_2/\text{CO} = 20/80$), reaction time 1 h for cyclohexylamine and 2 h for aniline.

^b Carbamate = methyl-N-cyclohexyl carbamate or methyl-N-phenyl carbamate.

^c Urea = N,N'-dicyclohexyl urea or N,N'-diphenyl urea.

as well as the investigation of various factors affecting the carbonylation of aniline and cyclohexylamine.

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