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Oxidative Carbonylation of Aromatic Amines by Selenium Compounds

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Various factors affecting the oxidative carbonylation of aromatic amines were investigated in the presence of a catalyst system comprising SeO_2 and alkali metal carbonate. An active catalyst, K_2SeO_3 was obtained from the reaction of SeO_2 and K_2CO_3 in methanol and the activity was tested. The effects of added alkali metal salts, solvents, aromatic amine substrates, molar ratio of aniline to catalyst, temperature, and pressure on the catalytic activity were studied. The activation energy of the carbonylation of aniline was evaluated as 17.0 kcal/mol. The highest turnover frequency was found to be 2082/h at aniline/catalyst = 12,800. A plausible mechanism for the carbonylation of aniline to diphenyl urea and phenyl carbamate has also been proposed. © 1999 Academic Press

1. INTRODUCTION

Carbamates are important materials as precursors for preparing isocyanates since they produce isocyanates and alcohols in good yields by thermal cracking (1, 2). Carbamates are commercially manufactured by reacting phosgene with the corresponding primary amine (3). Unfortunately, this conventional process possesses several disadvantages such as the use of highly toxic phosgene, the formation of large quantities of corrosive hydrogen chloride as a secondary product, and, furthermore, the presence of difficult-to-remove hydrolyzable chlorine compounds. Accordingly, there have been numerous attempts to produce carbamates by using non-phosgene methods (4–10). One of the approaches is the catalytic oxidative carbonylation of an amine with carbon monoxide and oxygen in the presence of an alcohol and an appropriate catalyst. A number of effective catalyst systems have been reported for preparing carbamates via oxidative carbonylation of amines (11–13). Group 8–10 transition metals and copper are commonly used catalysts for this purpose (14–16). Selenium and selenium compounds have also been demonstrated as catalysts in the carbonylation of aliphatic and alicyclic amines, but the catalysts show extremely low activity toward the carbonylation of aromatic amines (17–18).

In the previous communication, we reported that a catalyst comprising SeO_2 and alkali metal carbonate was highly effective for the oxidative carbonylation of aniline to produce phenyl carbamate and diphenyl urea as illustrated in Eqs. [1–3] (19).

$$2RNH_2 + CO + \frac{1}{2}O_2 \rightarrow RNHC(=O)NHR + H_2O, \quad [1]$$

$$RNHC(=O)NHR + R'OH \rightarrow RNH_2 + RNHC(=O)OR', \quad [2]$$

$$RNH_2 + CO + \frac{1}{2}O_2 + R'OH \rightarrow RNHC(=O)OR' + H_2O, \quad [3]$$

($R = $ phenyl, $R' = C_1$–C_4).

The synthesis of substituted ureas has also been extensively studied due to their importance in the chemical industry as precursors of carbamates, pigments, and resins, and the non-phosgene methods for converting substituted ureas to the corresponding carbamates are well established in the literature (20–23).

In this paper, various aspects of the oxidative carbonylations of aromatic amines are investigated by using a new catalyst system comprising SeO_2 and alkali metal carbonate, and a plausible mechanism is presented.

2. EXPERIMENTALS

2.1. *Chemicals*

Amines, selenium metal, selenium dioxide, and alkali metal carbonates were purchased from Aldrich Chemical Co. and used without further purification. Solvents were all reagent grade and distilled from appropriate drying agents under a nitrogen atmosphere prior to use. Over 99% purity of carbon monoxide and oxygen were obtained from Samsung Fine Chemical Co. and Daesung Oxygen Co., respectively.

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0021-9517/99 $30.00

2.2. *Instrumentation*

Gas chromatographic analyses were made for both gas and liquid samples. Gas samples were analyzed using a Gow-Mac gas chromatography equipped with a thermal conductivity detector and a Carbosphere column (6 ft). Liquid samples were analyzed using a Young-In 680D gas chromatography equipped with a flame ionization detector and a HP-1 capillary column (0.32 μm × 50 m). Mass spectral analyses were carried out employing a HP 5890A GC/HP 5917A MS detector. Urea analysis was carried out on a Waters HPLC using 4.6 × 150 mm Hyersil ODS column and UV detector (254 nm). Shimadzu (XRD 6000) diffractometer with a nickel-filtered Cu $K\alpha$ excitation source was employed to obtain XRD patterns for all the catalyst samples. The X-ray source was operated at 30 kV and 40 mA with scanning rate 2°/min. Compound identification was accomplished by the comparison of measured spectra of the samples with those of reference samples or JCPDS powder diffraction file data.

2.3. *Carbonylation Reaction*

All carbonylation reactions were conducted in a Parr 100 or 300 ml stainless steel bomb with a magnetic drive stirrer and an electrical heater. Reactions were carried out at 1000 rpm stirring rates to minimize mass transfer of O_2/CO mixture gas as a limitation to the reaction rates. Toluene was used as an internal standard due to the presence of high boiling insoluble materials in the reaction mixture, such as urea. The reactor was purged with nitrogen followed with O_2/CO mixture gas and then pressurized to about 4.08 MPa with O_2/CO mixture (molar ratio of $O_2/CO = 20/80$). The bomb was then heated with agitation to a specified reaction temperature with the addition of O_2/CO mixture gas from a reservoir tank (ballast tank) to maintain a specified pressure. The drop in pressure in the ballast tank was recorded by means of a pressure transducer and a recorder, which provides a convenient method for observing the progress of the reaction. After the reaction, the bomb was cooled to room temperature. Product mixtures were analyzed by GC, HPLC, and GC–MS. Solid catalyst mixtures were characterized by XRD.

2.4. *Alcoholysis of N,N′-Diphenyl Urea*

2.4.1. Under N_2 atmosphere. A 100 ml stainless Parr reactor was charged with 20 mmol diphenyl urea, 25 ml methanol, 1 g toluene as an internal standard, and catalyst (SeO_2/K_2CO_3). The reactor was purged with nitrogen and then heated to 130 or 170°C with agitation. After 2 h of reaction, the bomb was cooled to room temperature and the product mixture was analyzed by GC and HPLC.

2.4.2. Under (O_2/CO) pressure. A 100 ml stainless Parr reactor was charged with 20 mmol diphenyl urea, 25 ml methanol, 1 g toluene as an internal standard, and catalyst (SeO_2/K_2CO_3). The reactor was purged with nitrogen and then with O_2/CO mixture gas and was then pressurized to about 4.08 MPa with O_2/CO mixture (molar ratio of $O_2/CO = 20/80$). The bomb was then heated with agitation to a specified reaction temperature (130 or 170°C) with the addition of O_2/CO mixture gas from a reservoir tank. After the reaction, the bomb was cooled to room temperature and vented, and the product mixture was removed for analysis.

2.5. Synthesis of K_2SeO_3. In a 100 ml 3-neck flask, K_2CO_3 (40 mmol) was reacted with SeO_2 (40 mmol) dissolved in 25 ml methanol at room temperature for 1 h. As soon as the K_2CO_3 was added to the methanolic solution of SeO_2, CO_2 started to evolve. Removal of the solvent in vacuum gave a white solid. The white compound was characterized as K_2SeO_3 by elemental analysis [found, Se (38.1%), K (37.8%); calculated, Se (38.5%), K (38.5%)] and XRD results after several recrystallizations from diethyl ether/methanol solvent (yield: 87%).

3. RESULTS AND DISCUSSION

SeO_2-catalyzed oxidative carbonylations of aromatic amines were performed in various solvents in the presence of an alkali metal carbonate promoter. The effects of promoter, substrate, temperature, and pressure of O_2/CO on the carbonylation of aniline were evaluated.

In order to ensure that the catalyst retains its original activity, several experiments on the reusability of the catalyst were carried out.

A plausible reaction mechanism of the oxidative carbonylation of aniline catalyzed by K_2SeO_3 was also proposed.

3.1. *Effect of Added Alkali Metal Salt*

SeO_2-catalyzed oxidative carbonylation of aniline was carried out in the presence of various alkali metal salts. The reactions were performed in methanol at 130°C and 6.80 MPa ($O_2/CO = 20/80$) and the results are listed in Table 1. The addition of alkali metal halide, nitrite, nitrate, or sulfate was found to be ineffective for the carbonylation of aniline. Unlike other alkali metal salts, the presence of the alkali metal carbonate enabled the carbonylation of aniline to proceed very rapidly. Among the alkali metal carbonate, the activity was found in the order $SeO_2/Cs_2CO_3 \cong SeO_2/Rb_2CO_3 > SeO_2/K_2CO_3 > SeO_2/Na_2CO_3 > SeO_2/Li_2CO_3$, suggesting that the solubility and basicity of alkali metal carbonate might play an important role (19). It is interesting to note that only alkali metal carbonate is the active promoter among the alkali metal salt tested. It is presumed that the reaction of SeO_2 with alkali metal salts such as halide, nitrite, nitrate, and sulfate may not produce active alkali metal containing selenium

TABLE 1

Effect of Alkali Metal Salts on the Oxidative Carbonylation of Aniline[a]

Catalyst	Alkali metal salts	Conversion (%)	Selectivity (%)	
			Carbamate[b]	Urea[c]
SeO_2	None	N.R.		
SeO_2	KBr	N.R.		
SeO_2	KI	N.R.		
SeO_2	KNO_3	N.R.		
SeO_2	KNO_2	N.R.		
SeO_2	K_2SO_4	N.R.		
SeO_2	K_2CO_3	97.5	49.2	50.3
$K_2Se_2O_5$	None	95.4	27.2	72.0
K_2SeO_3	None	95.0	30.5	68.8
SeO_2	K_2CO_3/KI[d]	67.1	9.5	80.4
SeO_2	K_2CO_3/K_2SO_4[e]	63.4	8.4	78.6

[a] Conditions: aniline 40 mmol, SeO_2 0.2 mmol, K_2CO_3 1 mmol, methanol 25 ml, toluene 1 g (internal standard), temperature 130°C, pressure 6.80 MPa ($O_2/CO = 20/80$), reaction time 2 h.

[b] Carbamate: methyl-*N*-phenyl carbamate.

[c] Urea: *N*,*N*′-diphenyl urea.

[d] KI 0.2 mmol.

[e] K_2SO_4 0.2 mmol.

compound. Another possibility is that halide, nitrite, nitrate, or sulfate anion left in the catalyst or reaction mixture may act as a detrimental poison. In fact, the activity of a catalyst composed of SeO_2 and K_2CO_3 was decreased significantly by the addition of K_2SO_4 or KI.

3.2. *Alkali Metal Containing Selenium Compounds*

We reported that the reaction of K_2CO_3 with 2 equiv of SeO_2 in methanol produced $KSeO_2(OCH_3)$ and $K_2Se_2O_5$ (19). K_2SeO_3 was similarly prepared by the 1 : 1 reaction of K_2CO_3 with SeO_2 in methanol and the compound was characterized by XRD and elemental analysis. As shown in Fig. 1, the XRD pattern is in good agreement with that of K_2SeO_3 in the JCPDS Handbook. SeO_2 reacts with methanol to give $(CH_3O)Se({=}O)(OH)$ and $(CH_3O)_2Se(OH)_2$ (19), and the subsequent reaction of K_2CO_3 with equivalent of $(CH_3O)_2Se(OH)_2$ would produce K_2SeO_3 as in Eqs. [4–7]:

$$SeO_2 + CH_3OH \rightarrow (CH_3O)Se({=}O)(OH), \quad [4]$$

$$(CH_3O)Se({=}O)(OH) + CH_3OH \rightarrow (CH_3O)_2Se(OH)_2, \quad [5]$$

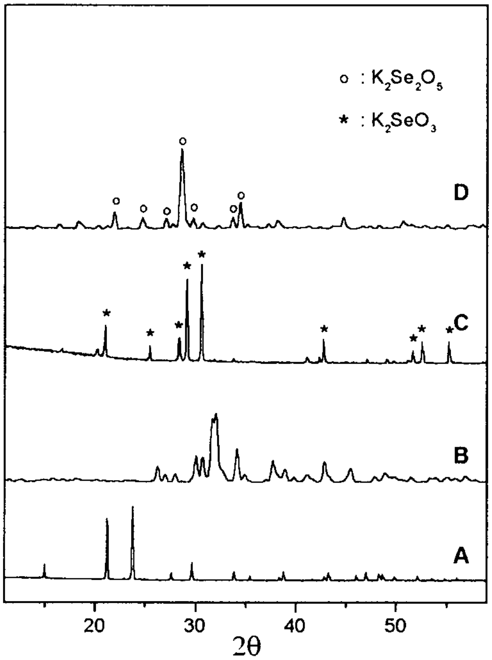
$$(CH_3O)_2Se(OH)_2 + K_2CO_3 \rightarrow (CH_3O)_2Se(OK)_2 + H_2O + CO_2, \quad [6]$$

$$(CH_3O)_2Se(OK)_2 \rightarrow K_2SeO_3 + (CH_3)_2O. \quad [7]$$

Like $K_2Se_2O_5$, K_2SeO_3 also showed the similar activity to the catalyst composed of SeO_2 and K_2CO_3 in the carbonylation of aniline, implying that both K_2SeO_3 and $K_2Se_2O_5$ may act as active species. The role of alkali metal carbonate and the reason for the activity of alkali metal containing selenium compound in the oxidative carbonylation of aromatic amine is described in the previous communication (19).

3.3. *Effect of Solvent*

Table 2 shows the effect of solvent on the conversion of aniline. In nonpolar solvents like *n*-hexane, benzene, and toluene, aniline was not carbonylated at all in the presence of a catalyst consisting of SeO_2 and K_2CO_3 ($K_2CO_3/SeO_2 = 5$), while in polar solvents like methanol, ethanol, isopropyl alcohol, *n*-propanol, *sec*-butyl alcohol, THF, and DMF, high conversion of aniline was obtained. It is surprising to note that $K_2Se_2O_5$ and K_2SeO_3, ionic products obtained from the reactions of SeO_2 and K_2CO_3 in methanol, were able to carbonylate aniline even in nonpolar solvents such as *n*-hexane, benzene, and toluene. These results strongly indicate that the active species are ionic and the formation of such ionic active species is favored in polar solvent. Surprisingly, unlike in other C_1–C_4 alcohol, the catalyst comprising SeO_2 and K_2CO_3 showed very little activity in *tert*-butyl alcohol solvent, and it is believed that the steric hindrance of *tert*-butyl alcohol prohibits the formation of active species such as $K_2Se_2O_5$ and K_2SeO_3. This is supported by the experimental result that the reaction by $K_2Se_2O_5$ and K_2SeO_3



A. SeO_2 B. K_2CO_3 C. $SeO_2 + K_2CO_3$ D. $2\,SeO_2 + K_2CO_3$

FIG. 1. XRD patterns of A–D.

TABLE 2

Effect of Solvents on the Oxidative Carbonylation of Aniline[a]

Catalyst	Solvent	Conversion (%)	Selectivity (%)	
			Carbamate[b]	Urea[c]
SeO_2/K_2CO_3	Methanol	97.5	49.2	50.3
SeO_2/K_2CO_3	Ethanol	95.7	35.2	63.4
SeO_2/K_2CO_3	*n*-Propanol	94.6	15.3	83.7
SeO_2/K_2CO_3	Isopropyl alcohol	92.8	9.1	89.7
SeO_2/K_2CO_3	*sec*-Butyl alcohol	91.4	2.1	96.8
SeO_2/K_2CO_3	THF	96.7	—	98.8
SeO_2/K_2CO_3	DMF	95.4	—	98.6
SeO_2/K_2CO_3	*tert*-Butyl alcohol	1.1	tr.	—
SeO_2/K_2CO_3	*n*-Hexane	N.R.		
SeO_2/K_2CO_3	Benzene	N.R.		
SeO_2/K_2CO_3	Toluene	N.R.		
K_2SeO_3	*tert*-Butyl alcohol	97.8	0.9	98.1
K_2SeO_3	Toluene	80.4	—	98.6
K_2SeO_3	Benzene	85.6	—	98.5

[a] Conditions: aniline 40 mmol, SeO_2 0.2 mmol, K_2CO_3 1 mmol, solvent 25 ml, toluene 1 g (internal standard), temperature 130°C, pressure 6.80 MPa ($O_2/CO = 20/80$), reaction time 2 h.

[b] Carbamate: methyl-*N*-phenyl carbamate.

[c] Urea: N,N'-diphenyl urea.

in *tert*-butyl alcohol proceeded as fast as in other C_1–C_4 alcohols. In separate experiments, the reaction of SeO_2 with K_2CO_3 in THF and DMF at room temperature also produced K-containing selenium compounds by elemental and XRD analyses, but the full characterization of these compounds was not successful. Like $K_2Se_2O_5$ and K_2SeO_3, these unidentified compounds also show high catalytic activity for the carbonylation of aniline in nonpolar solvents, again supporting the assumption that the nature of active species is ionic and such ionic active species are favorably formed in polar solvents.

3.4. *Effect of Substrate*

SeO_2-catalyzed oxidative carbonylations of aniline and substituted anilines were performed in methanol at 130°C in the presence of a promoter, K_2CO_3. As shown in Table 3, aniline, *o*-toluidine, dimethyl anilines, 2,4,6-trimethylaniline, 2,4-diaminotoluene, and 4,4′-methylenedianiline were carbonylated to give high yields of corresponding carbamates and/or ureas while *p*-nitroaniline was not carbonylated at all under the same experimental condition. Relatively higher yield of carbamate was obtained in the carbonylation of aniline, but ureas were predominantly formed in the case of substituted aniline, possibly due to the electronic effect of substituents. It is not clear at the moment why the carbonylation of *p*-nitroaniline did not take place. However, it is likely that nitro group in *p*-nitroaniline played a certain role in quenching the catalytic activity of SeO_2/K_2CO_3. Experimental results also show that the catalyst comprising SeO_2 and K_2CO_3 catalyst was inactive toward the reductive and oxidative carbonylations of nitrobenzene that were carried out in methanol at 130°C for 2 h.

The carbonylation of aromatic diamine such as 2,4-diaminotoluene and 4,4′-methylenedianiline is important in the chemical industry because the resulting carbonylated products, diurea and/or dicarbamate, can be directly used as intermediates of TDI (toluene diisocyanate) and MDI (methylenediphenyl diisocyanate).

3.5. *Effect of Molar Ratio of Aniline/SeO_2*

The effect of molar ratio of aniline/SeO_2 on the carbonylation of aniline was studied in the presence of SeO_2/K_2CO_3 at 130°C ($K_2CO_3/SeO_2 = 5$) and 6.80 MPa ($O_2/CO = 20/80$). The molar ratio of aniline to SeO_2 was varied in the range 50–25,600, and the results are shown in Fig. 2. The conversion of aniline remained almost constant at around 95% in the molar ratio range between 50 and 1600, and thereafter sharp decrease in conversion was observed. The selectivity of carbamate decreased as the molar ratio increased, whereas the selectivity of diphenyl urea increased with the increasing molar ratio. The maximum turnover frequency was found to be 2082/h at molar ratio of 12,800, indicating that our catalyst system comprising SeO_2 and K_2CO_3 is as active as Pd system reported by Fukuoka *et al.* (14).

3.6. *Effect of Temperature and Pressure*

Figures 3 and 4 show the effects of temperature and pressure on the oxidative carbonylation of aniline to give phenyl carbamate and diphenyl urea in the temperature range 90–170°C at various pressure of O_2/CO (molar ratio of $O_2/CO = 20/80$) ranging from 2.04 to 6.80 MPa. A plot of

TABLE 3

Oxidative Carbonylation of Various Aromatic Amines[a]

Amine	Conversion (%)	Selectivity (%)	
		Carbamate[b]	Urea[c]
Aniline	97.5	49.2	50.3
o-Toluidine	96.4	23.4	75.3
4,4′-Methylenedianiline	95.2	0.5	98.1
2,4-Diaminotoluene	94.1	0.4	98.7
2,4-Dimethylaniline	98.9	tr.	98.6
2,6-Dimethylaniline	99.1	tr.	98.1
2,4,6-Trimethylaniline	97.6	tr.	99.1
p-Nitroaniline	N.R.		
p-Nitroaniline[d]	N.R.		
Nitrobenzene	N.R.		
Nitrobenzene[d]	N.R.		

[a] Conditions: substrate 40 mmol, SeO_2 0.2 mmol, K_2CO_3 1 mmol, methanol 25 ml, toluene 1 g (internal standard), temperature 130°C, pressure 6.80 MPa ($O_2/CO = 20/80$), reaction time 2 h.

[b] Carbamate: methyl-*N*-phenyl carbamate.

[c] Urea: N,N'-diphenyl urea.

[d] Reactions carried out in the absence of O_2, pressure 6.80 MPa.

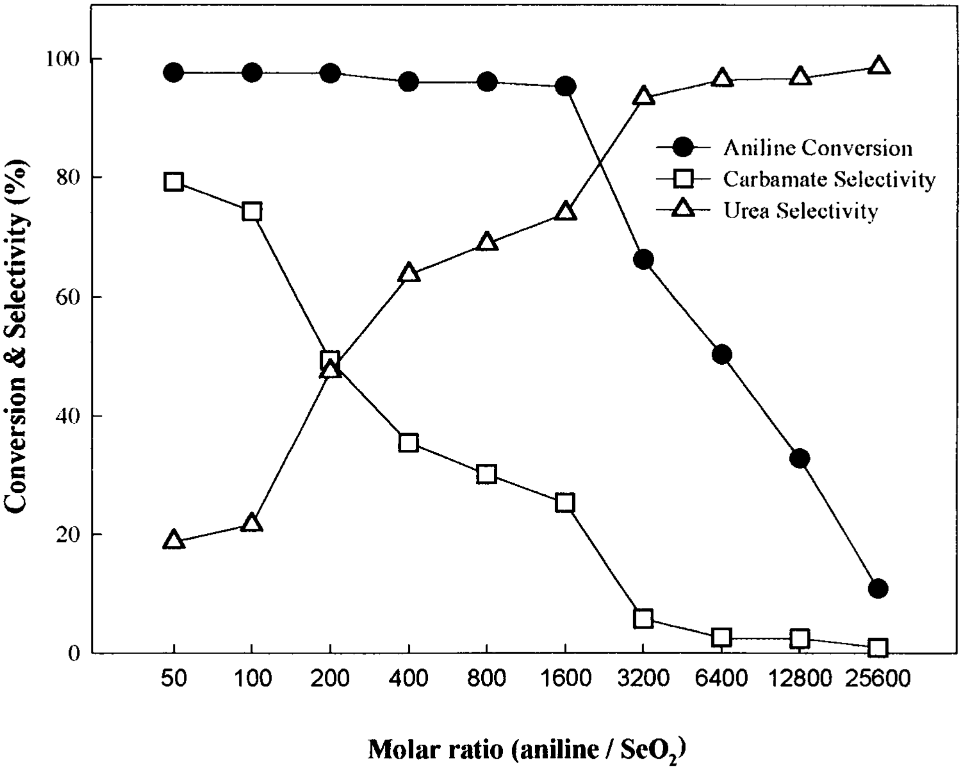


FIG. 2. Effect of molar ratio (aniline/SeO_2) on the oxidative carbonylation of aniline. Conditions: aniline 40 mmol, molar ratio ($K_2CO_3/SeO_2 = 5$), methanol 25 ml, toluene 1 g, temperature 130°C, pressure 6.80 MPa ($O_2/CO = 20/80$), reaction time 2 h. Carbamate, methyl-*N*-phenyl carbamate; urea, *N*,*N*′-diphenyl urea.

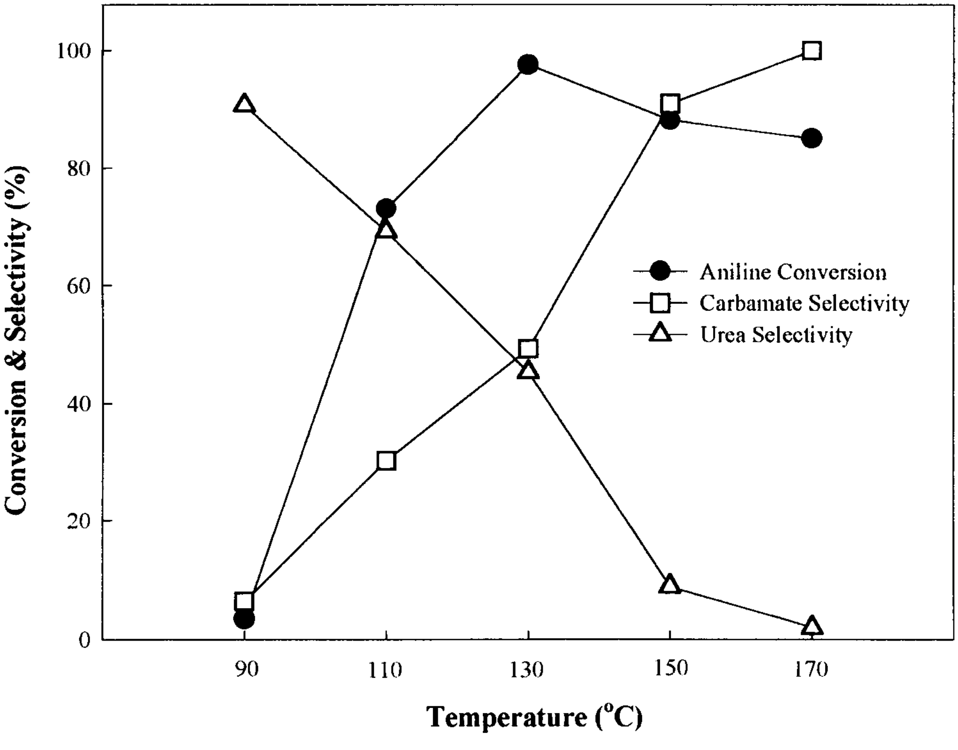


FIG. 3. Effect of temperature on the oxidative carbonylation of aniline. Conditions: aniline 40 mmol, SeO_2 0.2 mmol, K_2CO_3 1 mmol, methanol 25 ml, toluene 1 g, pressure 6.80 MPa, reaction time 2 h. Carbamate, methyl-*N*-phenyl carbamate; urea, *N*,*N*′-diphenyl urea.

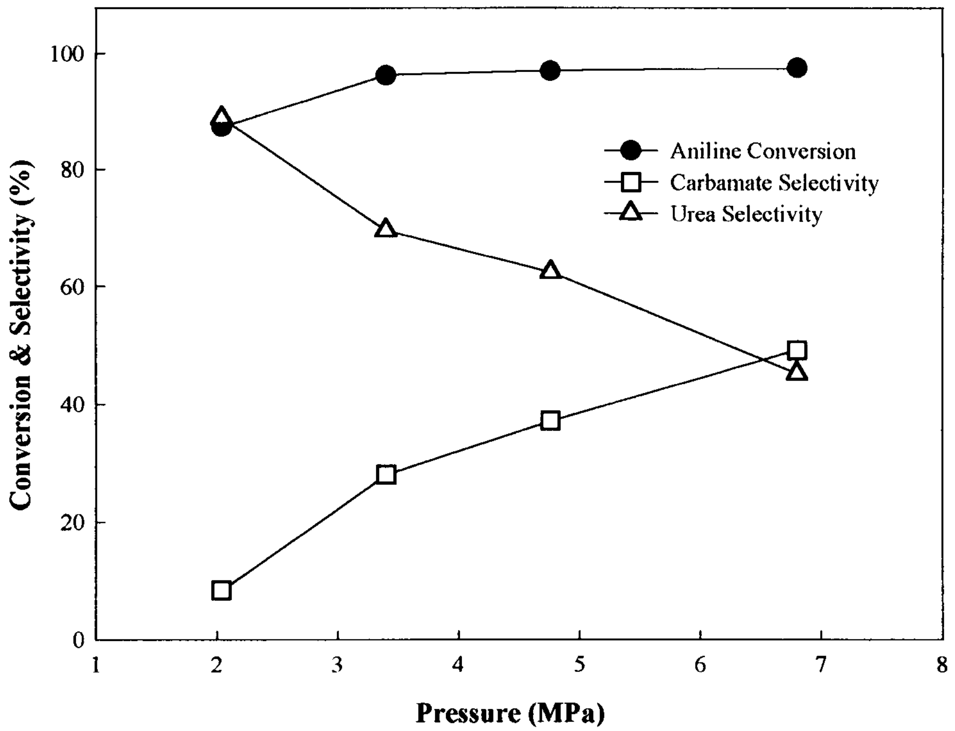


FIG. 4. Effect of pressure on the oxidative carbonylation of aniline. Conditions: aniline 40 mmol, SeO_2 0.2 mmol, K_2CO_3 1 mmol, methanol 25 ml, toluene 1 g, temperature 130°C, reaction time 2 h. Carbamate, methyl-*N*-phenyl carbamate; urea, *N*,*N*′-diphenyl urea.

—log rate vs $1/T$ is shown in Fig. 5, from which the value of activation energy, E_a, was evaluated as 17.0 kcal/mol.

The conversion of aniline increased with increasing temperature up to 130°C and then decreased with further increase in temperature. The decrease in conversion at temperatures higher than 130°C can be rationalized by assuming that the rate of alcoholysis of diphenyl urea is higher than that of carbonylation of aniline, i.e., the rate

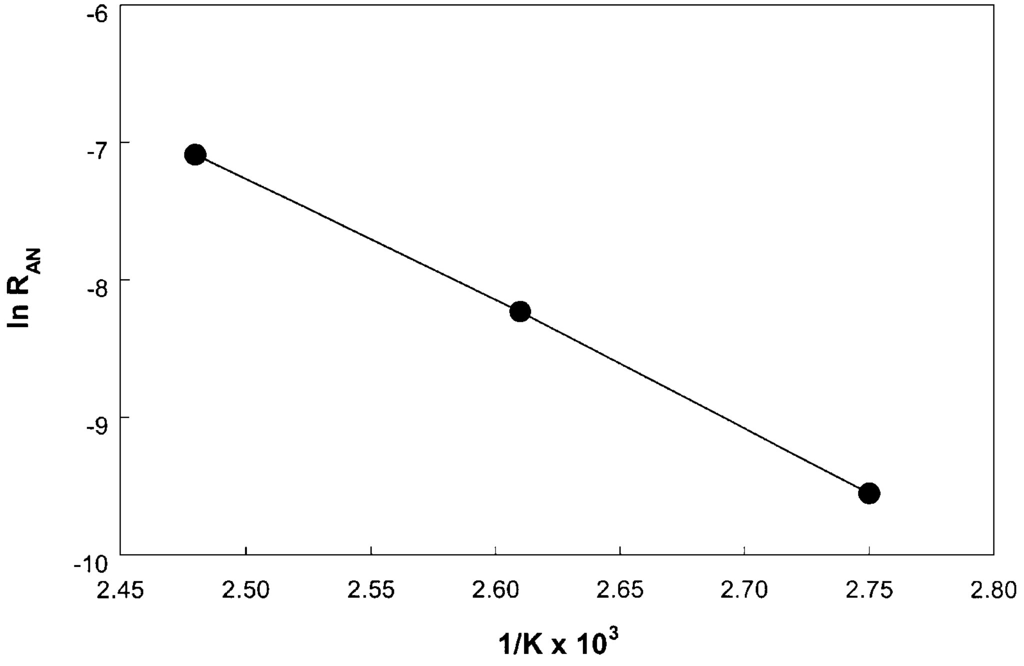


FIG. 5. Arrhenius plot.

TABLE 4

Alcoholysis of N,N'-Diphenyl Urea[a]

Pressure (MPa)	Temp. (°C)	Conversion (%)	Selectivity (%)	
			Carbamate[b]	Aniline
0.1 (N_2)	130	60.5	49.2	50.4
0.1 (N_2)	170	96.2	49.2	50.5
6.80 (O_2/CO)	130	25.5	82.8	16.7
6.80 (O_2/CO)	170	67.5	75.9	23.7

[a] Conditions: N,N'-diphenyl urea 20 mmol, SeO_2 0.2 mmol, K_2CO_3 1 mmol, methanol 25 ml, toluene 1 g (internal standard), $O_2/CO = 20/80$, reaction time 2 h.

[b] Carbamate: methyl-N-phenyl carbamate.

of formation of aniline from diphenyl urea is higher than that of aniline disappearance by carbonylation at higher temperature (see Eqs. [1–3]). The results on the alcoholysis of diphenyl urea at 130°C and 170°C are listed in Table 4. Table 4 shows that under atmospheric pressure of N_2 at 130°C, the 60.5% of diphenyl urea was converted into aniline and phenyl carbamate. When the reaction was conducted at 6.80 MPa of O_2/CO, however, the conversion dropped significantly from 60.5% to 25.5%. Such a pressure effect was also observed by Macho *et al.* (4). The selectivity of phenyl carbamate increased with the increase of temperature while the selectivity of diphenyl urea decreased, strongly indicating that diphenyl urea is an intermediate to the formation of phenyl carbamate. The effect of pressure on the conversion of aniline as shown in Fig. 4 seems to be less pronounced than that of temperature because the conversion reached over 85% as long as the pressure was maintained above 2.04 MPa of O_2/CO ($O_2/CO = 20/80$). However, the selectivity of phenyl carbamate was found to be more strongly dependent on the pressure as going from 8% at 2.04 MPa to 49% at 6.80 MPa even though the dependence was much less pronounced compared with that of temperature. In order to test the catalyst reusuability, the carbonylation reaction was performed for 2 h in the presence of a catalyst, SeO_2/K_2CO_3 at 130°C and 6.80 MPa of O_2/CO in methanol. After the reaction, the reaction solution was filtered to remove insoluble diphenyl urea. The resulting solution containing the catalyst was reused with a fresh charge of aniline. It was found that the catalyst retained its original activity even after four reuses.

3.7. *Effect of CO_2*

The catalytic activity of SeO_2/K_2CO_3 was tested for the oxidation of CO to CO_2, and the effect of CO_2 on the oxidative carbonylation of aniline was investigated.

It is reported that oxidation of CO to CO_2 takes place during the oxidative carbonylation of amines (24). As most of the catalysts proposed in the literature, our catalyst system, SeO_2/K_2CO_3, also showed some catalytic activity toward the oxidation of CO to CO_2. The oxidative carbonylation of aniline (40 mmol) was performed in methanol (25 ml) at 130°C and 6.80 MPa ($O_2/CO = 20/80$) for 2 h. GC analysis of gas sample showed that 7.7% of CO consumed was oxidized to CO_2. Conversion of aniline and selectivity to methyl-N-phenyl carbamate were 97.5% and 49.2%, respectively. In order to find out the effect of CO_2 formation on the carbonylation of aniline, the carbonylation reaction was conducted in the presence of added CO_2 using 6.80 MPa of $CO_2/O_2/CO$ mixture gas ($CO_2/O_2/CO = 12/18/70$) instead of O_2/CO ($O_2/CO = 20/80$). Gas chromatographic analysis of liquid sample gave 98.1% of conversion and 48.3% of selectivity, which were similar to those obtained from the above experiment performed without the presence of added CO_2.

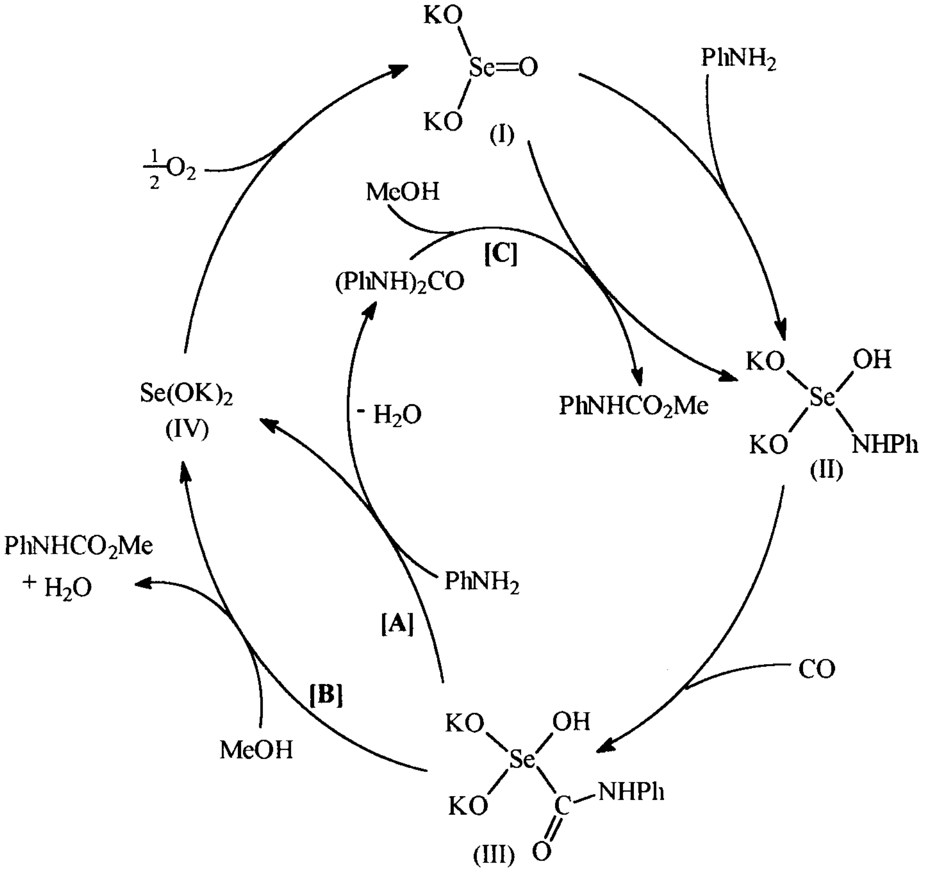
From these results, it is concluded that the oxidation of CO to CO_2 occurs in significant yield, but the effect of CO_2 formation on the carbonylation of aniline can be neglected.

3.8. *Proposed Mechanism*

Based on the experimental results, the mechanism of the oxidative carbonylation of aniline catalyzed by K_2SeO_3 is proposed in Scheme 1. As described in the experimental section, the active species, K_2SeO_3 is formed by the reaction of SeO_2 with K_2CO_3. In a second step, aniline reacts with K_2SeO_3 to give amido complex **II**. Amido species **II** could take up one molecule of CO to form selenium carbonyl species, $Se(OK)_2(CO)(OH)(NHPh)$, and the subsequent insertion of CO into Se–N bond would produce carbamoyl complex **III**. The formation of carbamoyl species **III** seems to be a key step in the proposed mechanism. Addition of one molecule of another aniline to species **III** and the subsequent elimination of diphenyl urea and H_2O give rise to selenium species **IV** (path A). **IV** can also be produced by interaction of species **III** with one molecule of methanol and subsequent elimination of phenyl carbamate and H_2O (path B). Liberated diphenyl urea can be added to **I**, forming $Se(OK)_2(OH)(NPhCONHPh)$, which, in turn, reacts with methanol to give phenyl carbamate, simultaneously regenerating species **II** (path C). The final step is the regeneration of K_2SeO_3 (**I**) by the interaction of species **IV** with molecular O_2. Even though diphenyl urea was found to be easily converted into phenyl carbamate by reacting with methanol in the presence of SeO_2/K_2CO_3 catalyst, it cannot be concluded that diphenyl urea is the sole intermediate to the formation of phenyl carbamate. Phenyl carbamate also can be produced directly via a separate route such as path B other than the diphenyl urea route.

4. CONCLUSIONS

Various factors affecting the oxidative carbonylation of aromatic amines were investigated in the presence of a new



SCHEME 1. A plausible reaction mechanism of oxidative carbonylation of aniline catalyzed by K_2SeO_3.

catalyst system comprising SeO_2 and alkali metal carbonate. The reaction of SeO_2 with K_2CO_3 in methanol produced active alkali metal containing selenium compounds, K_2SeO_3 and $K_2Se_2O_5$. The carbonylation reactions catalyzed by SeO_2/K_2CO_3 proceeded in polar solvents, like C_1–C_4 alcohols, THF, and DMF, but not in nonpolar solvents such as *n*-hexane, benzene, and toluene. In contrast with SeO_2/K_2CO_3 catalyst, the use of alkali metal containing selenium compounds, K_2SeO_3 and $K_2Se_2O_5$, resulted in a high conversion of aniline, irrespective of the polarity of the solvent used. The activation energy calculated from the Arrhenius plot was evaluated as 17.0 kcal/mol, and the maximum turnover frequency was found to be 2082/h at 130°C with a molar ratio of aniline/$SeO_2 = 12{,}800$. The formation of phenyl carbamate was more strongly dependent on the temperature than on the pressure. A plausible reaction mechanism has been discussed.

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