Tellurium-catalyzed Carbonylation of Amines with Carbon Monoxide[1)]

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Carbonylation of amines with carbon monoxide was catalyzed by tellurium to produce corresponding urea derivatives, formamides, and molecular hydrogen. The urea formation proceeds according to the equation; $2RNH_2+CO \rightarrow (RNH)_2CO+H_2$. The successful achievement of the catalytic formation of urea derivatives would be due to the thermal instability of hydrogen telluride which decomposes to generate elemental tellurium and hydrogen. The formation of formamides and hydrogen was found to be suppressed by the addition of nitrobenzene which did not affect the urea formation. Effects of the reaction time, temperature, pressure of carbon monoxide, and additives on this carbonylation reaction are discussed.

Carbonylation of amines with carbon monoxide to produce urea derivatives by the use of S,[2)] Se,[3)] $Fe(CO)_5$,[4)] AgOAc,[5)] and inorganic oxidizing agents[6)] has been known to proceed as stoichiometric reaction. On the other hand, in order to carry out this carbonylation catalytically many studies have been done to show the effectiveness of Se,[3)] transition metals, and their complexes of Hg,[7)] Mn,[8)] Fe,[9)], Co,[10)] Ni,[11)] Rh,[12)] Pd,[13)] W,[14)] Pt.[15)]

The reaction of primary amines with carbon monoxide in the presence of sulfur gave corresponding urea derivatives and hydrogen sulfide[2)] (Reaction 1).

$$2\,RNH_2 + CO + S \longrightarrow (RNH)_2CO + H_2S \qquad (1)$$

This reaction gave moderate yields of ureas based on sulfur used, and it required high temperature and high pressure of carbon monoxide.

In contrast to the above sulfur dependent reaction, under mild reaction conditions selenium[3)] catalyzed the carbonylation of various amines with carbon monoxide and oxygen to afford quantitative yields of urea derivatives with high selectivity (Reaction 2). This

$$2\,RR'NH + CO + \frac{1}{2}O_2 \xrightarrow[\text{r. t., 1 atm}]{\text{Se}} (RR'N)_2CO + H_2O \qquad (2)$$

reaction was shown to consist of the carbonylation reaction (Reaction 3), and the oxidative regeneration of the catalyst (Reaction 4).

$$2\,RR'NH + CO + Se \longrightarrow (RR'N)_2CO + H_2Se \qquad (3)$$

$$H_2Se + \frac{1}{2}O_2 \longrightarrow Se + H_2O \qquad (4)$$

In the periodic table, tellurium belongs to the same VIa group as oxygen, sulfur, and selenium. The present paper describes the novel carbonylation of amines with carbon monoxide catalyzed by elemental tellurium. The tellurium-catalyzed carbonylation is shown characteristically in the simplest mode to form the equimolar amounts of ureas and molecular hydrogen (Reaction 5). In this reaction, the formation

$$2\,RNH_2 + CO \xrightarrow{\text{Te}} (RNH)_2CO + H_2 \qquad (5)$$

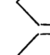
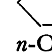
of formamide derivatives was found to occur (Reaction 6).

$$RNH_2 + CO \longrightarrow RNHCHO \qquad (6)$$

Results and Discussion

General Reactions. Butylamine, octylamine, cyclohexylamine, and benzylamine were examined for this carbonylation reaction. The results are shown in Table 1. The equimolar amounts of ureas and molecular hydrogen were obtained (Reaction 5). Un-

Table 1. Tellurium-catalyzed carbonylation[a)] of amines with CO

Run	Amine (100 mmol)	Te (mmol)	Time / h	Urea (mmol)	H_2 (mmol)	Formamide (mmol)
1	*n*-$BuNH_2$	1	10	7.6	7.1	10.0
2	*n*-$BuNH_2$	1	10	7.7	7.4	15.3
3	*n*-$BuNH_2$	1	10	7.4	7.0	12.5
4	*n*-$BuNH_2$	1	10	7.8	7.2	17.3
5	*n*-$BuNH_2$	0.05	10	2.9	2.9	1.3
6	*n*-$BuNH_2$	1	72	22.0	21.0	51.8
7	*n*-$BuNH_2$	0	10	0.01	0.04	0.3
8	 -NH_2	1	10	4.1	3.3	7.2
9	 -NH_2[b)]	1	72	12.1	12.2	37.1
10	*n*-$OctNH_2$	1	10	2.3	1.9	1.0
11	*n*-$OctNH_2$[c)]	1	72	10.0	d)	24.8
12	$PhCH_2NH_2$	1	10	4.7	5.0	1.1

a) Temp: 140 °C, CO: 30 kg/cm². b) Cyclohexylamine: 85.1 mmol (10 ml). c) Octylamine: 60.2 mmol (10 ml). d) Not determined.

less otherwise noted, 1 mmol of tellurium was always used, and thus the yields of products (in mmol) correspond to the turnover numbers. For all amines, the carbonylation reaction proceeded catalytically. The turnover number for the urea formation in Run 5 in Table 1, for example, corresponded to 5.8 per hour.

The reaction of butylamine with carbon monoxide in the presence of tellurium catalyst was carried out four times under the identical reaction conditions. The reproducibility of the formation of 1,3-dibutylurea and hydrogen was satisfactory (Runs 1—4). The reproducibility using octylamine and cyclohexylamine was also confirmed fairly good by duplicated experiments. In regard to the reproducibility of formamide formation, the yields varied much more than those of the urea derivatives and hydrogen.

In the reaction performed for 72 h, almost all butylamine was consumed to give urea and formamide derivatives (Run 6). The mass balance in the carbonylation of octylamine was confirmed nearly 100% (Run 11).

Dialkylamines such as diethylamine and dimethylamine failed to react resulting in the recovery of the starting materials. Ammonia and aniline were also unreactive under similar conditions.

Effects of Temperature and CO Pressure. The yields of 1,3-dibutylurea increased as the temperature was elevated, whereas plots of the yields of hydrogen and *N*-butylformamide showed the maxima around at 160 °C (Fig. 1). The temperature higher than 100 °C was required for the effective performance of the catalytic reaction. The change of the reaction temperature caused the similar effects both on the hydrogen formation and the formamide formation. This fact seemed very suggestive. That is, in both reactions the same species would play important roles; which was hydrogen telluride we tentatively considered.

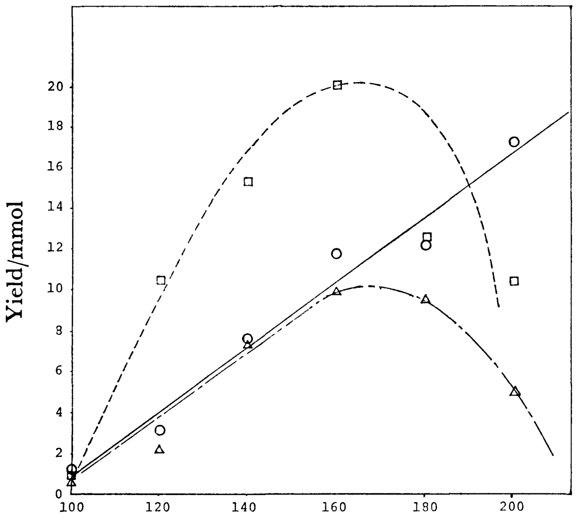


Fig. 1. Effect of temperature on tellurium-catalyzed carbonylation of amines with carbon monoxide. Tellurium: 1 mmol, butylamine: 100 mmol, carbon monoxide: 30 kg/cm², time: 10 h. —○—: 1,3-Dibutylurea, —△—: hydrogen, —□—: *N*-butylformamide.

The higher pressure of carbon monoxide was advantageous for all the formation of 1,3-dibutylurea, hydrogen, and *N*-butylformamide (Fig. 2). But it should be noted that the formamide formation was more sensitive to the pressure than the others.

Effects of Additives. We have reported that nitrobenzene was reduced with hydrogen telluride generated *in situ* from aluminum telluride and water.[16] Evidently, the addition of nitrobenzene to the present tellurium-catalyzed carbonylation system gave aniline in good yield, resulting in the drastic suppression of the formation of hydrogen and *N*-butylformamide (Run 2 in Table 2). The value of the reaction constant, ρ, of the Hammett equation for the concurrent reduction of nitrobenzenes in the tellurium-catalyzed carbonylation system was obtained as +0.8. These results might suggest the presence of hydrogen telluride in this carbonylation. The reaction would proceed as shown in Scheme 1.

Comparison of the Catalyses by Se and Te in the Urea Formation Reaction. We have reported[3] that carbonylation reaction of amines in the presence of selenium afforded stoichiometric amounts of urea derivatives and hydrogen selenide (Reaction 3). By use of selenium under the typical reaction conditions at 140 °C for 10 h, the carbonylation was carried out in a glass

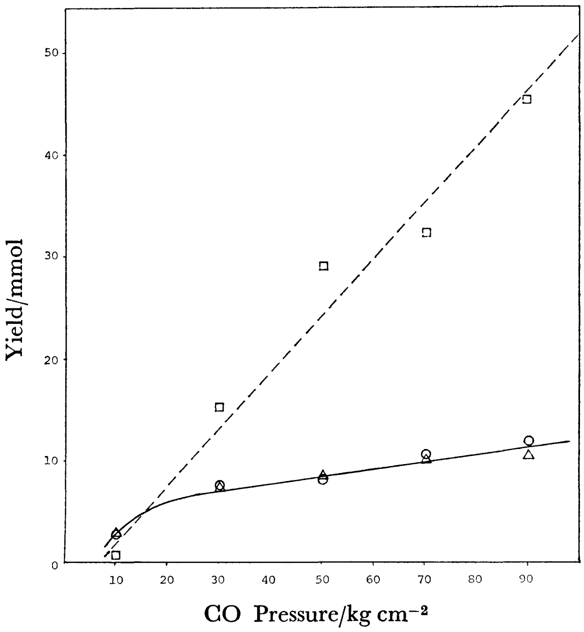
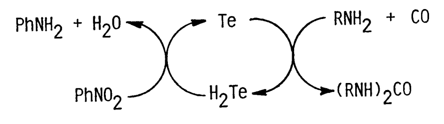


Fig. 2. Effect of CO pressure on tellurium-catalyzed carbonylation of amines with carbon monoxide. Tellurium: 1 mmol, butylamine: 100 mmol, temperature: 140 °C, time: 10 h. —○—: 1,3-Dibutylurea, —△—: hydrogen, —□—: *N*-butylformamide.



Scheme 1. Tellurium-catalyzed carbonylation of amines with carbon monoxide in the presence of nitrobenzene.

TABLE 2. CONTROLLED EXPERIMENTS[a)]

Run	Te (mmol)	Additive (mmol)	$\frac{\text{Time}}{\text{h}}$	Urea (mmol)	H_2 (mmol)	Formamide (mmol)	$PhNH_2$ (mmol)
1	1	—	72	22.0	21.0	51.8	—
2[b)]	1	$PhNO_2$: 10	72	15.9	1.3	2.0	9.0
3	1	—	10	7.6	7.1	10.1	—
4	1	Se : 1	10	19.1	14.5	28.7	—
5	0	Se : 1	10	1.2	0.8	10.6	—

a) n-$BuNH_2$: 100 mmol (10 ml), Temp: 140 °C, CO: 30 kg/cm^2. b) Unreacted nitrobenzene was not detected after the reaction.

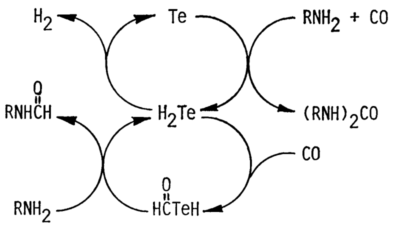
tube inserted in an autoclave. This reaction gave the stoichiometric amount of 1,3-dibutylurea to the used selenium with little formation of hydrogen. When this inserted glass tube was not used, more than equimolar amount of urea to selenium catalyst was produced (Run 5 in Table 2). This result would be attributed to the wall effect of the autoclave. In the tellurium-catalyzed carbonylation, no wall effect was observed on the contrary. These results show the similarity and the difference in the catalyses by selenium and tellurium; both non-transition metal elements, selenium and tellurium, catalyze the carbonylation of amines with carbon monoxide, where the former requires suitable oxidizing agents such as oxygen to give water, while the latter does not with the production of hydrogen. With regard to the reaction conditions, the selenium-catalyzed urea synthesis was achieved under much milder conditions than the other.

A Plausible Reaction Path. At present, we don't have enough evidence to propose the precise reaction mechanism. But some of the results mentioned above may help us to describe the plausible carbonylation path by tellurium catalyst, referring to the accumulated knowledge on selenium catalyzed carbonylation. From a close analogy to the selenium chemistry,[3)] tellurium catalyzed urea formation (Reaction 5) would be best explained by the assumption that it consists of two reactions: one, the stoichiometric reaction of amines, carbon monoxide, and tellurium to produce ureas and hydrogen telluride (Reaction 7); the other, the dehydrogenative decomposition of hydrogen telluride to molecular hydrogen and activated tellurium (Reaction 8). The assumption of the intermediacy of hydrogen telluride in this reaction does not contradict the following evidences. i) Pure hydrogen telluride was prepared by the reaction of aluminum telluride and water. Thus prepared hydrogen telluride was found to decompose quite readily to its components, molecular hydrogen and tellurium (Reaction 8). This may be due to the weak bond energy between hydrogen and tellurium reported as 64 kcal/mol.[17)] Therefore hydrogen telluride may well be the precursor of hydrogen and tellurium catalyst. ii) The equimolar formation of ureas and hydrogen should be well accounted for by the Reaction 5. iii) The formylation of nitrogen-hydrogen bond with carbon monoxide was also mentioned in the catalysis by the triethylammonium salt of hydrogen selenide at elevated temperature under CO pressure similar to the present reaction conditions.[18)] The formation of formamides was observed in the tellurium catalyst system (see Table 1 and Reaction 6). These results might be also due to the catalysis of hydrogen telluride. iv) There was found a similar tendency in the temperature effects on the yields of hydrogen and formamides (Fig. 1). The same species, which we suppose is hydrogen telluride, might be responsible for it. v) The addition of nitrobenzene into the tellurium catalyzed carbonylation system gave important results as mentioned already; a) no effect on the urea formation, b) the drastic suppression on the formation of molecular hydrogen and formamides, c) the production of aniline, as the reduced form of nitrobenzene.

$$2\,RNH_2 + CO + Te \longrightarrow (RNH_2)CO + H_2Te \qquad (7)$$

$$H_2Te \longrightarrow H_2 + Te \qquad (8)$$

In conclusion a probable reaction path could be represented as shown in Scheme 2.



Scheme 2. A plausible reaction path for the tellurium-catalyzed carbonylation of amines with carbon monoxide.

The intermediacy of tellurol formic acid, $H\overset{O}{\overset{\|}{C}}TeH$,[19)] in the formamide formation reaction is still a subject to be solved.

Experimental

Instruments. Melting points were measured with a Yanagimoto Micro Melting Point apparatus. IR spectra were taken with a Shimadzu IR-400. NMR spectra (60 MHz) were recorded on a Hitachi R-24 B. Mass spectra were recorded on a Hitachi mass spectrometer, Model RMU-6E. Analytical gas chromatography was performed with a Shimadzu 3BT with thermal conductivity detector, Shimadzu 3BF and GC-6A both with flame ionization detector.

Apparatus. All carbonylations were carried out using 50 ml stainless steel autoclaves (SUS-304) purchased from Taiatsu Glass Kogyo. In order to eliminate the wall effect, the reaction was carried out in a glass tube inserted in the autoclave.

Materials. Butylamine, cyclohexylamine, octylamine, and benzylamine were purchased from Nakarai Kagaku, and purified by distillation from KOH just before use. Tellurium lump (99.999%) was obtained from Wako Junyaku. Tellurium was powdered by use of agate mortar and pestle and stored under dry nitrogen in the absence of light. The reactive gray tellurium had to be used within a few weeks, since it gradually turned black becoming inactive for the carbonylation under similar conditions. Carbon monoxide (99.99%) was purchased from Neriki Gas in a cylinder and used without any purification. CO pressure mentioned in this paper refers to that at room temperature.

Product Analysis. The analysis of the gas phase after the reaction was performed with a Shimadzu 3BT gas chromatograph using a 3.3 m×3 mm stainless steel column packed with 30—60 mesh molecular sieves 5A and nitrogen effluent gas at 150 °C of the oven temperature. The analytical error of hydrogen was less than 2%. 1,3-Dibutylurea was analyzed on a Shimadzu GC-6A using a 70 cm×3 mm glass column packed with 3% DEGS on acid-washed, base-treated, DMCS-treated, 80—100 mesh Shimalite W at 150 °C of the oven temperature, and diethyl phthalate was used as an internal standard. Formamides, nitrobenzenes, and anilines were analyzed using a 3.3 m×3 mm stainless steel column packed with 25% PEG-20M on acid-washed, 60—80 mesh Shimalite W at 200 °C of the oven temperature, and dodecane was used as an internal standard. 1,3-Dicyclohexylurea, 1,3-dioctylurea, and 1,3-dibenzylurea were obtained after the removal of unreacted amines and formed formamides from the reaction mixtures under reduced pressure. Identifications were made based on spectroscopic data (IR, NMR, and Mass measurements). Melting points were in good agreement with those[20] of authentic samples.

Carbonylation of Butylamine (Run 1 Table 1). In the autoclave were placed tellurium (1 mmol, 128 mg), butylamine (100 mmol, 10 ml), and a magnetic stirring bar. The autoclave was flushed with carbon monoxide three times and charged at 30 kg/cm^2. The autoclave was sunk in an oil bath maintained at 140 °C, and the reaction was conducted for 10 h with magnetic stirring. After the reaction, the autoclave was immediately cooled to room temperature with cold water. Then the resulting gas was collected in a gas sampler. The VPC analysis of the gas revealed to contain 7.1 mmol of molecular hydrogen. The reaction mixture was transferred into a 100 ml flask and was allowed to contact with air for 30 min with magnetic stirring in order to precipitate tellurium. Products were obtained after the removal of deposited tellurium followed by the evaporation of the unreacted butylamine. From GLPC analyses, 1,3-dibutylurea and *N*-butylformamide were found to be produced in the yields of 7.6 mmol and 10.1 mmol, respectively. 1,3-Dibutylurea was recrystallized from hexane.

Carbonylation of Octylamine (Run 11 in Table 1). Similarly, the carbonylation of octylamine (60.2 mmol, 10 ml) was carried out. 1,3-Dioctylurea was produced as crystals (2.48 g, 10.0 mmol). *N*-Octylformamide (114—120 °C/4 mmHg, 3.90 g, 24.8 mmol) and unreacted octylamine (54—57 °C/10 mmHg, 1.68 g 13.0 mmol) were obtained after fractionation.

Carbonylation of Butylamine by Te in the Presence of Nitrobenzene. In the autoclave tellurium (1 mmol, 128 mg), butylamine (100 mmol, 10 ml), and nitrobenzene (10 mmol, 123 mg) were placed with a magnetic stirring bar. The autoclave was then flushed with carbon monoxide three times and charged at 30 kg/cm^2. The reaction was conducted at 140 °C for 72 h with vigorous stirring. After the reaction, resulting gas was analyzed by VPC, and 1.3 mmol of hydrogen was found to be formed. GLPC analyses of the reaction mixture, after the removal of tellurium, showed the formation of 15.9 mmol of 1,3-dibutylurea and 2.0 mmol of *N*-butylformamide. Neither 1-butyl-3-phenylurea nor 1,3-diphenylurea was detected.

Competitive Reduction of Nitrobenzene and p-*Nitrotoluene in This Carbonylation System.* The autoclave was charged with tellurium (1 mmol, 128 mg), butylamine (100 mmol, 10 ml), nitrobenzene (5 mmol, 615 mg), *p*-nitrotoluene (5 mmol, 685 mg), and carbon monoxide (30 kg/cm^2). After the reaction at 140 °C for 72 h, deposited tellurium was removed by filtration. GLPC analyses of the filtrate revealed that 2.48 mmol of aniline and 1.81 mmol of *p*-toluidine were formed.

Carbonylation of Butylamine by Selenium Using a Glass Tube. Into a glass tube inserted in the autoclave were placed selenium (1 mmol, 79 mg), butylamine (100 mmol, 10 ml), and a magnetic stirring bar. The apparatus was charged with carbon monoxide at 30 kg/cm^2. After the reaction at 140 °C for 10 h, the resulting gas was collected in a gas sampler, and little amount of hydrogen was detected by VPC analysis. The resulting mixture was transferred into a 100 ml flask and the oxidation with air at room temperature for 1 h precipitated selenium. Products were obtained by the removal of selenium followed by the evaporation of the solvent. GLPC analyses of the products showed the formation of 1.0 mmol of 1,3-dibutylurea and 1.5 mmol of *N*-butylformamide.

Generation of Pure Hydrogen Telluride. In a 100 ml three-necked glass vessel equipped with a 10 ml dropping funnel, a stopper, and a connection tube to a trapping vessel maintained at −196 °C, was placed powdered aluminum telluride (29 g, 66 mmol) under nitrogen atmosphere. All the apparatus was covered with aluminum foil to eliminate the effect of light. Then, 10 ml of water was dropped very slowly into the reaction vessel over a period of 1 h. The reaction was exothermic, so the reaction vessel should be cooled with ice. Hydrogen telluride was trapped at −196 °C as a white solid. When warmed to −78 °C, hydrogen telluride began to decompose. As the temperature was slowly elevated, hydrogen telluride decomposed below its melting point of −51 °C and gray tellurium remained.

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19) In the triethylammonium salt of hydrogen selenide ($Et_3N\cdot H_2Se$) catalyzed formylation of aromatic amines under similar reaction conditions as present ones, the intermediacy of selenol formic acid, $H\overset{\overset{O}{\|}}{C}SeH$, was considered; see Ref. 18.

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