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A New and Convenient Process for Separation of Carbon Monoxide

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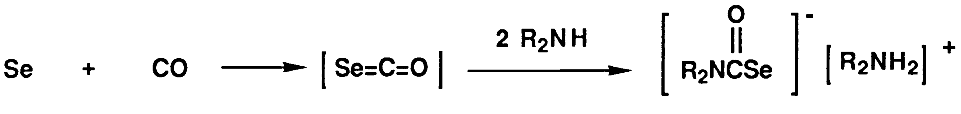
A new method for the efficient separation of carbon monoxide from a binary mixture of carbon monoxide and hydrogen has been established by use of a selenium/secondary amine reaction system. This system consists of the selective uptake of carbon monoxide by the reaction with selenium and secondary amines to form the corresponding ammonium carbamoselenoates (**1**) in solution and the release of carbon monoxide by thermolysis of **1** into starting components. The amount of separated carbon monoxide was stoichiometric and the purity was higher than 99.9%.

In relation to the growing importance of carbon monoxide as a key material for the synthesis of a variety of basic chemicals especially in C 1 chemistry,(1) much attention has been paid to the development of efficient and practical methods for the separation of carbon monoxide from gas mixtures such as synthesis gas, blast furnace gas, and coke-oven gas which contain N_2, CO_2, CH_4, H_2, H_2O etc. (as components or impurities). The most frequently employed for this purpose are Copper liquor and cryogenic separation systems.(2) Recently several new processes using Cu(I) based solid state adsorbents have been proposed by Hirai and co-workers(3) and by some other groups.(4) In this communication, we wish to describe a unique separation method of carbon monoxide based on the reversible reaction of selenium, carbon monoxide, and secondary amines.

During the course of our study on the selenium-assisted carbonylation of amines,(5) we have found that selenium reacts with amines and carbon monoxide to give the corresponding ammonium carbamoselenoates **1** under mild conditions.



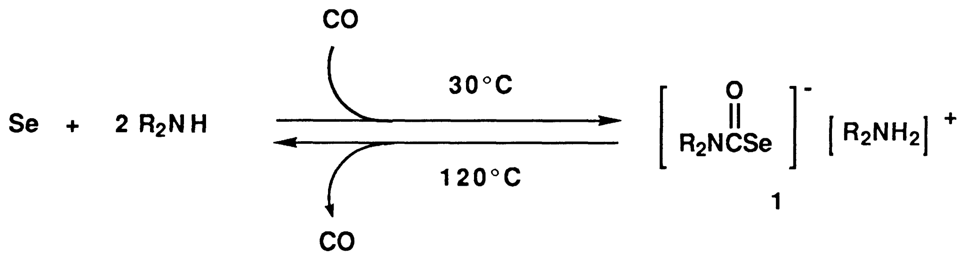
$$\mathrm{Se} + \mathrm{CO} \longrightarrow [\mathrm{Se{=}C{=}O}] \xrightarrow{2\,R_2NH} \left[R_2N\overset{\overset{O}{\|}}{C}Se\right]^- [R_2NH_2]^+ \qquad (1)$$

1

This reaction has been explained by the nucleophilic attack of an amine molecule to the carbon atom of transiently formed carbonyl selenide (Se=C=O) as shown in Eq. 1. Recent studies on the reactivity and the stability of these salts have revealed that **1** derived from secondary amines do not react further when oxygen is not present in the reaction system.[6)]

$$\mathbf{1} \xrightarrow{\text{heat}} \mathrm{CO} + \mathrm{Se} + 2\,\mathrm{R_2NH} \tag{2}$$

On the other hand, we have found that ammonium salts **1** derived from secondary amines are thermally unstable and easily decompose upon heating to selenium, carbon monoxide, and free amines (Eq. 2). For example, when a homogeneous solution of **1b** (R=n-Pr) in an excess amount of dipropylamine, prepared by stirring a mixture of metallic selenium (2,40 g, 30 mmol) and dipropylamine (150 mmol, 20.6 mL) under carbon monoxide at 25 °C for 18 h, was heated, vigorous decomposition was observed during a range of 96-98 °C releasing pure carbon monoxide and a stoichiometric amount of elemental selenium. Similar experiments using diethylamine, di-isopropylamine, and dibutylamine showed that **1a** (R=Et), **1c** (R=i-Pr), and **1d** (R=n-Bu) decomposed during the ranges of 86-89 °C, 57-59 °C, and 93-95 °C, respectively. These results, together with the fact that **1** do not decompose at room temperature even when carbon monoxide was purged in vacuo, suggest that the enthalpy change (ΔS) of the reaction depicted in Scheme 1 is sufficiently large in negative, as can be expected from the stoichiometry, and that the equilibrium shifts to the right on heating by changing the ΔG (= $\Delta H - T \cdot \Delta S$) positive. This is a very important feature of this reaction system for the separation of carbon monoxide in sufficiently pure form by a single operation (*vide infra*).



Scheme 1. A novel system for separation of carbon monoxide.

These successful preliminary results led us to attempt the separation of carbon monoxide from a binary mixture of carbon monoxide and hydrogen having a composition similar to that of synthesis gas. A typical experiment is as follows.

In a stainless-steel autoclave, were placed selenium (30 mmol, 2.40 g) and dipropylamine (150 mmol, 20.6 mL). The autoclave was charged with a binary mixture gas to 30 kg/cm^2 at 25 °C comprising 20.6 kg/cm^2 (44.8 mmol) of CO and 9.4 kg/cm^2 (20.5 mmol) of H_2. After stirring at 25 °C for 3 h, the autoclave was depressurized and the gas was introduced into a balloon. Gas chromatographic analysis of the gas collected in the balloon showed that it contained 13.1 mmol of CO and 21.2 mmol of H_2. Then the gas remaining in the autoclave was purged under reduced pressure in order to avoid the contamination with it. The resulting solution in the autoclave was then heated slowly and maintained at 120 °C for about 2 h until the gas evolution ceased. The gas evolved was collected and analyzed by a similar way, showing that 32.2 mmol of carbon monoxide with a purity of 99.9% was released by the thermolysis which was stoichiometric for the amount of selenium used. The results obtained by using several secondary amines are summarized in Table 1.

Table 1. Separation of CO by Using Se-R_2NH Reaction System[a)]

Run	Amine	Carbon monoxide		Selenium
		recovered %[b,c)]	purity %[b)]	recovered %[c)]
1	n-Pr_2NH	100	99.9	98.6
2[d)]		100	99.9	99.6
3[e)]		100	99.9	99.2
4	n-Bu_2NH	94	99.9	96.6
5	i-Pr_2NH	24	99.9	96.3

a) Se (30 mmol, 2.40 g), R_2NH (150 mmol), CO (20.6 kg/cm^2), H_2 (9.4 kg/cm^2), 25 °C, 3 h. Thermolysis was performed by heating the resulting solution gradually up to 120 °C.
b) Analyzed by gas chromatography (Molecular Sieves 5A, 2.9 m, 100 °C). c) Based on selenium used.
d) Water (1 mmol) was added. e) Water (2 mmol) was added.

In any cases, purity of the reproduced carbon monoxide was higher than 99.9% and nearly all of the selenium and the amines used were recovered.[7)] When diisopropylamine was used, carbon monoxide was absorbed in a less amount than the amount of selenium used, probably because the formation of **1c** was a slow process due to the steric effect and was incomplete under the conditions employed (Run 5). As shown in Runs 2 and 3, addition of a small amount of water did not affect these reactions. It was also confirmed that the resulting heterogeneous mixture of selenium and amine could be used repeatedly without any purification. Furthermore, aprotic solvents such as toluene, xylene and 1,4-dioxane could be used as solvent. This system was also applicable to the gas mixtures containing other components rather than hydrogen which are inert in this reaction system such as N_2 and CH_4.

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7) Removal of deposited selenium by filtration followed by evaporation of the dipropylamine gave ca. 170 mg of oily residue containing $n\text{-}Pr_2NCHO$, $(n\text{-}Pr_2N)_2CO$ and $(n\text{-}Pr_2NCOSe)_2$.

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