

### Preliminary communication

## COPPER-PROMOTED DEOXYGENATION OF CARBON DIOXIDE BY ISOCYANIDE

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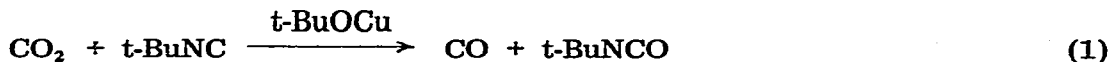
### Summary

Copper(I) *t*-butoxide-promoted deoxygenation of carbon dioxide by *t*-butyl isocyanide to produce carbon monoxide and *t*-butyl isocyanate is described.

Interest in organic reactions of CO<sub>2</sub> caused by a transition metal complex is increasing rapidly. Exploration of organic reactions of CO<sub>2</sub> other than carboxylation is important. Several examples of preparation of a transition metal—carbonyl complex using CO<sub>2</sub> have been reported [1]. Very recently, we have found reversible CO<sub>2</sub> fixation by copper(I) *t*-butoxide [2]. *t*-BuOCu absorbs CO<sub>2</sub> in the



presence of 3 equivalents of *t*-BuNC in benzene at ambient temperature to form an isolable complex, *t*-BuOCO<sub>2</sub>Cu·(CNBu-*t*)<sub>3</sub> (I). On refluxing a benzene solution of I under a stream of nitrogen, quantitative decarboxylation takes place. We now report an interesting reaction pattern of *t*-BuOCu-promoted deoxygenation of CO<sub>2</sub> by *t*-BuNC to produce CO and *t*-BuNCO at higher temperature. Heating I at 100–150°C in a closed system also effected the reaction. Thus, I functions as a carrier of activated CO<sub>2</sub>.



In a 100 or 200 ml closed flask, the isolated complex I (0.1–0.5 mmol) or a mixture of *t*-BuOCu (0.1–0.6 mmol)/3 *t*-BuNC/CO<sub>2</sub> in 5 ml of mesitylene or tetralin was heated at 100–150°C under nitrogen. The results of GLC analyses of the gaseous products are summarized in Fig. 1. It is found that *t*-BuOCu converted CO<sub>2</sub> into CO in the presence of *t*-BuNC at higher temperature. No reaction took place without *t*-BuOCu. Expt. 1 in Fig. 1 shows that at 130°C I evolved CO<sub>2</sub> quantitatively which was gradually converted to CO. This finding means that the reaction using the isolated complex I becomes equivalent to that of *t*-BuOCu/3 *t*-BuNC/CO<sub>2</sub> at 130°C. In this sense, I acts as a carrier of activated

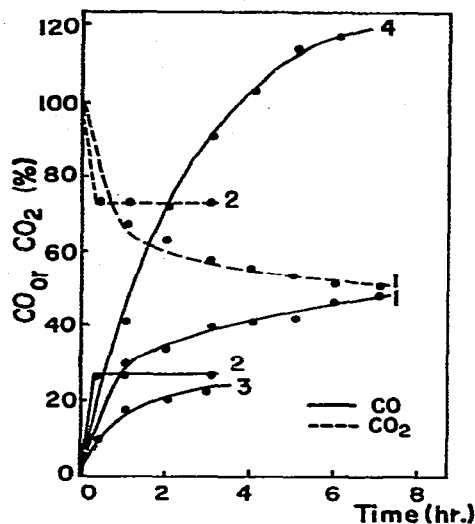


Fig. 1. CO gas formation and CO<sub>2</sub> gas evolution (% based on copper). 1. I (0.481 mmol), 130°C, mesitylene. 2. I (0.409 mmol), 150°C, tetralin. 3. t-BuOCu (0.562 mmol)/3 t-BuNC/CO<sub>2</sub>, 100°C, tetralin. 4. t-BuOCu (0.500 mmol)/5 t-BuNC, under CO<sub>2</sub> atmosphere, 120°C, mesitylene.

CO<sub>2</sub>. Reaction of I at 150°C caused the decomposition of the copper complex to produce metallic copper and the composition of gaseous products reached a constant value immediately after the reaction was initiated. When an excess of CO<sub>2</sub> was used, the reaction proceeded more effectively. The reaction of t-BuOCu (0.500 mmol)/5 t-BuNC at 120°C for 5 h under CO<sub>2</sub> atmosphere (CO<sub>2</sub>/Cu ca. 14) produced CO in 114% based on copper (expt. 4).

Addition of n-butyl alcohol to a reaction mixture at ambient temperature after heating for the requisite time produced t-BuNHCO<sub>2</sub>Bu-n. The yield of urethane based on copper was equal to that of CO. For example, the reaction under CO<sub>2</sub> atmosphere (t-BuOCu (0.136 mmol)/5 t-BuNC, 120°C, 3 h, in tetralin, CO<sub>2</sub>/Cu ca. 82) produced 119% CO and 116% urethane.

These findings suggest that CO<sub>2</sub> underwent deoxygenation by t-BuNC to form CO and t-BuNCO in the coordination sphere of copper (eq. 1). t-BuOCu forms a stable 1:1 complex with t-BuNC even in the presence of an excess of t-BuNC. The t-BuOCu·CO complex is known to release CO quantitatively on addition of t-BuNC to give t-BuOCu·CNBu-t [3]. Taking into consideration the complete decarboxylation of I at 130°C, it is probable that the key intermediate of the present reaction is a CO<sub>2</sub>-coordinated t-BuOCu·CNBu-t complex which also seems to be important in the formation of I at lower temperature.

t-BuOCu was the most effective among the copper(I) salts examined. CuCl, CuOAc and Cu<sub>2</sub>O were ineffective for the reaction. n-BuSCu was less effective. CO gas evolution was not observed in the system of t-BuOCu/3 P-n-Bu<sub>3</sub>/CO<sub>2</sub> at 100°C. Preparation of a transition metal carbonyl complex using CO<sub>2</sub> has been reported [1]. The present reaction is featured with the copper-promoted deoxygenation of CO<sub>2</sub> by isocyanide to produce a reactive organic intermediate, an isocyanate, together with the liberation of CO.

## References

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