

CARBONATE FORMATION BY THE REACTION OF CUPRIC METHOXIDE AND CARBON MONOXIDE

Takeo Saegusa, Tetsuo Tsuda, Katsuhiko Isayama and Kiyooki Nishijima

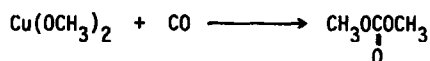
Department of Synthetic Chemistry, Faculty of Engineering,

Kyoto University, Kyoto, Japan

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Recently we have reported that urethane is formed by the reaction of thallic acetate, amine and carbon monoxide in methanol.¹⁾ In this reaction, carbomethoxythallic acetate was proposed as an essential intermediate. Cupric acetate also gives urethane in a similar reaction condition,¹⁾ and carbomethoxycupric compound may also be assumed as an intermediate.

These findings prompted us to examine the reaction between cupric methoxide and carbon monoxide. Now, it has been found that dimethyl carbonate is formed in the reaction of cupric methoxide and carbon monoxide carried out in pyridine.



In a 50 ml. stainless steel tube, cupric methoxide²⁾ and pyridine (solvent) were placed, to which carbon monoxide was compressed up to 80 kg./cm.² at -78°C. The tube was closed and was heated. Then carbon monoxide was purged off, and the reaction mixture was filtered and was distilled to isolate volatile matters at temperature up to 200°C under 1 mmHg. The distillate was collected and analyzed by gas chromatography. Dimethyl carbonate was obtained, which was identified by the comparison of the retention time of gas chromatography with the authentic sample. The results are shown in Table I.

It may be assumed that carbomethoxycupric compound (I) is first formed by the insertion of carbon monoxide into the copper-oxygen linkage, which decomposes to produce dimethyl carbonate. Here, bis(carbomethoxy)copper may also be assumed as another possible intermediate.

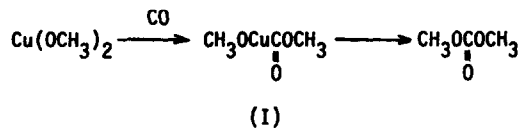



TABLE I. Reaction of Cupric Methoxide and Carbon Monoxide in Pyridine Solvent^{a)}



$\text{Cu}(\text{OCH}_3)_2$ (mmoles)	 (mmoles)	Reaction temp. (°C)	Reaction time (hr.)	Yield of dimethyl carbonate ^{b)} (%)
7.9	79	0	20	8
8.6	86	room temp.	48	31
8.2	82	70	20	42
4.9	49	110	23	14

a) In a pressure tube, CO gas was compressed up to 80 kg./cm.² at -78°C to a mixture of $\text{Cu}(\text{OCH}_3)_2$ and pyridine. The tube was closed and heated.

b) The yield of dimethyl carbonate is based on cupric methoxide.

The assumption of the intermediate of carbomethoxycupric compound is supported, at least partly, by the observation that the same reaction carried out in the presence of amine produces urethane. Piperidine was placed in a reaction tube together with cupric methoxide and pyridine (solvent), to which carbon monoxide was compressed up to 80 kg./cm.². Methyl 1-piperidine-carboxylate was formed and identified by the retention time of gas chromatography. The results are shown in Table II.

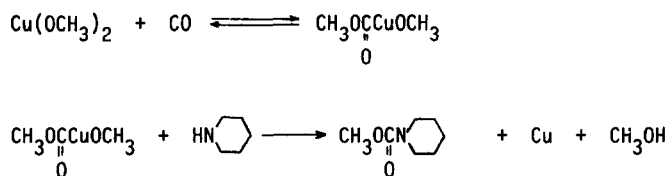
TABLE II. Reaction of Cupric Methoxide, Carbon Monoxide and Piperidine in Pyridine Solvent^{a)}

$\text{Cu}(\text{OCH}_3)_2$ (mmoles)	 (mmoles)	 (mmoles)	Temp. (°C)	Time (hr.)	Yield of Methyl 1-piperidine- carboxylate (%) ^{b)}
4.3	4.3	43	0	20	49
13.6	13.6	136	room temp.	43	33
6.4	6.4	64	60	20	66
4.6	4.6	46	110	23	56

a) Reactions were carried out by the same procedure as those in Table I except for the presence of piperidine.

b) The yield of methyl 1-piperidinecarboxylate is based on cupric methoxide.

Carbomethoxycupric compound may reasonably be included in the reaction scheme leading to the formation of methyl 1-piperidinecarboxylate.



For the urethane formation, the cupric methoxide procedure of the present study is superior to the previous one¹⁾ using cupric acetate, methanol, amine and carbon monoxide. For example, the cupric methoxide procedure yields urethane in a yield of 33 % at room temperature, whereas the cupric acetate-methanol procedure gives urethane in a yield of 9 %.¹⁾

The detailed mechanism of the formation of dimethyl carbonate has not been established. Elucidation of the combination of carbomethoxy and methoxy groups leading to dimethyl carbonate requires further studies. It seems important, however, that under the reaction conditions of the present study dimethyl oxalate has not been detected in the reaction products.

REFERENCES

- 1) T. Saegusa, T. Tsuda and K. Isayama, Tetrahedron Letters, in press.
- 2) C. H. Brubaker, Jr. and M. Wicholas, J. Inorg. Nucl. Chem., 27, 59 (1965).