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# A Novel Synthesis of Dimethyl Malonate by Carbonylation of Methyl Chloroacetate Catalyzed by Cobalt Complex

Wei Hong SONG, Xuan Zhen JIANG*

Department of Chemistry, Zhejiang University, Hangzhou 310027

**Abstract:** A novel method of preparing dimethyl malonate by carbonylation of methyl chloroacetate catalyzed by $Na[Co(CO)_4]$ was proposed. $Na[Co(CO)_4]$ was synthesized *in situ* in the presence of $Na_2S_2O_3$and iron powder. The effects of some reaction parameters such as temperature, CO pressure and the concentrations of catalyst on the yields of dimethyl malonate were discussed. The kinetic data were studied and a possible reaction mechanism was proposed.

**Keywords:** Dimethyl malonate, cobalt complex, carbonylation, reaction mechanism.

Dimethyl malonate (DMM) is an important organic synthesis intermediate. Traditional synthetic method by reaction of mono-chloroacetic acid with sodium cyanide[1] is poisonous and complicated. Therefore, an interest in green synthesis routes of DMM has risen greatly. The several processes for preparing DMM by carbonylation of methyl chloroacetate catalyzed by $Co_2(CO)_8$ have been reported[2~5]. However, $Co_2(CO)_8$ is unstable and must be prepared under high pressure (12 Mpa). Moreover, the yield of DMM was about 80% as reported by Kibayashi *et al* [2]. In this study, $Na[Co(CO)_4]$ synthesized *in situ* was employed as catalyst for carbonylation of methyl chloroacetate in high conversion (*ca*.97%), and DMM was obtained in both high selectivity (*ca*.99% ) and yield (*ca*.96%). The kinetic data was firstly reported here and the possible mechanism was also suggested. The reaction equation is as follows:

$$ClCH_2COOCH_3 \quad + \quad CO \quad + CH_3OH \xrightarrow[Et_3N]{Na[Co(CO)_4]} CH_2(COOCH_3)_2 \quad + \quad HCl$$

## Experimental

The $CoCl_2.6H_2O$ (3.0g) was heated to turn blue color before using, mixing with iron powder (0.5g), $Na_2S_2O_3$ (0.6g) and 150ml methanol, and then the mixture was added into an 500 ml autoclave rapidly. The apparatus was scavenged three times with CO and then a CO pressure of 1.0 Mpa was established. The mixture was stirred at 50℃ for 2 hr, then methyl chloroacetate (20 ml) and tertiary amine (40 ml) were pumped into the autoclave. The CO pressure and reaction temperature were increased to certain value. The mixture was further stirred for 6 hr. Progress of reaction was monitored by G.C.-FID (PEG-20M as a column). After the completion of the reaction, the mixture was filtered. DMM was obtained by vacuum distillation and identified by HP5973

(GC-MS).

## Results and Discussion

*Effects of temperature and pressure*

The effect of reaction temperature on the yields of DMM was presented in **Table 1** which showed that the yields of DMM increased with elevating temperature, the selectivity of DMM was fairly high as given in **Table 1**.

**Table 1** The effect of temperatures on the yield of DEM

| Temp. (℃) | $P_{CO}$ (Mpa) | Conv. (%) | Yield (%) | Select. (%) |
|---|---|---|---|---|
| 50 | 1.5 | 65.0 | 64.2 | 98.7 |
| 55 | 1.5 | 79.0 | 77.8 | 98.5 |
| 60 | 1.5 | 87.4 | 85.6 | 98.0 |
| 70 | 1.5 | 97.6 | 96.8 | 99.2 |

**Table 2** listed the effect of the CO pressure on the yield of DMM, it indicated that the CO pressure has almost no effect on both DMM yield and its selectivity.

**Table 2** The effect of CO pressures on the yields of DMM

| Temp.(℃) | $P_{CO}$ (Mpa) | Conv. (%) | Yield (%) | Select. (%) |
|---|---|---|---|---|
| 60 | 1.0 | 87.5 | 86.0 | 98.3 |
| 60 | 2.0 | 87.5 | 86.4 | 98.7 |
| 60 | 3.0 | 88.6 | 87.4 | 98.5 |
| 60 | 4.0 | 87.5 | 86.2 | 98.5 |

*Base effect*

Alkaline reagents were necessary as a scavenger of hydrogen chloride which was produced during reaction, we found that $Et_3N$ performed more effective than the other bases listed in **Table 3**.

**Table 3** The effect of different kind of bases on the yields of DMM

| Base | $Et_3N$ | $K_2CO_3$ | $NaHCO_3$ | $Na_2CO_3$ | NaOH |
|---|---|---|---|---|---|
| Conv. (%) | 99.8 | 50 | 58.5 | 65.2 | 100 |
| Yield (%) | 98.2 | 35.6 | 32.4 | 28.8 | 0 |
| Select. (%) | 98.5 | 71.2 | 55.4 | 44.2 | 0 |

Reaction temperature at 70℃, the pressure of CO at 1.0 MPa

**Table 4** The effect of the concentrations of catalyst on the yields of DMM

| Catalyst(mol/L)<br>Time (h) | 0.021<br>6 | 0.042<br>6 | 0.063<br>6 | 0.084<br>5 | 0.105<br>4 |
|---|---|---|---|---|---|
| Conv. (%) | 31.5 | 60.4 | 87.5 | 96.5 | 97.4 |
| Yield (%) | 30.0 | 58.8 | 86.0 | 95.2 | 96.8 |
| Select. (%) | 95.5 | 97.3 | 98.3 | 98.6 | 99.4 |

At Reaction temperature of 60℃, At CO pressure of 2.0 Mpa

*Catalyst concentration effect*

The yields of DMM were increased with the increase in the concentrations of catalyst as shown in **Table 4**. The TOF (turnover frequency) of catalyst was 2.62 $h^{-1}$.

### Kinetic Study and Possible Reaction Mechanism

The reaction kinetic equation was assumed as follows:

$$r = k\, P_{co}^{y}\, [\text{Cat.}]^{z}\, C^{x}$$

r: reaction rate k: Reaction rate constant. $P_{CO}$: Pressure of CO.
C: The concentration of methyl chloroacetate. x, y, z: Reaction order.

Keep the other reaction conditions constant, the initial concentration of methyl chloroacetate $C_0$ was 1.13 mol/L, we determined the variation of the concentration of DMM with the reaction time at different temperatures under constant CO pressure (2.0Mpa) and found that lnC showed a monotonous dependence on the reaction time as shown in **Figure 1**, indicating a pseudo-first-order reaction (*i.e.* x = 1). The apparent activation energy was determined from the Arrhenius plot presented in **Figure 2** with a value of 56.4 kJ/mol.

**Figure 1** Variation of lnC with reaction time
~ 50℃ ~ 60℃ Δ ~ 65℃ ~ 70℃

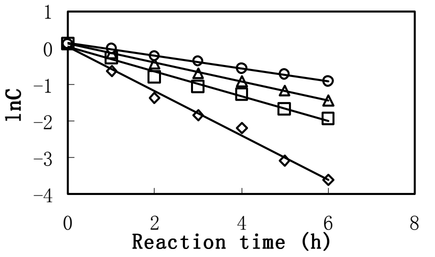
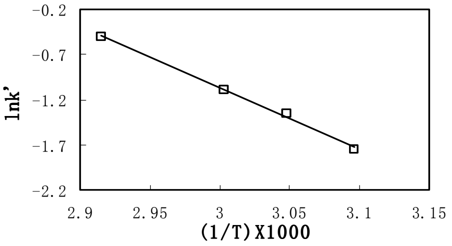


**Figure 2** Arrhenius Plot
$k' = k\, P_{co}^{y}\, [\text{Cat.}]^{z}$



The rate constant k' was measured under different pressure of CO (**Table 5**), it was found that the reaction rate constant k' ($k' = k\, P_{co}^{y}\, [\text{Cat.}]^{z}$ ) was approximately unchanged with variation of CO pressure (*i.e.* y = 0). Therefore, we can deduced $k' = k\, [\text{Cat.}]^{z}$.

**Table 5** The effect of the CO pressures on the reaction rates

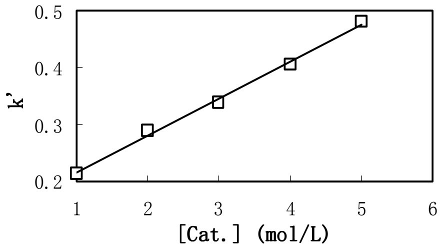
| Pressure of CO (Mpa) | 1.0 | 1.5 | 2.0 | 3.0 | 4.0 |
|---|---|---|---|---|---|
| k' ($k\, p_{co}^{y}\, [\text{Cat.}]^{z}$) | 0.3381 | 0.3325 | 0.3375 | 0.3335 | 0.3394 |

We also determined the relationship between rate constant k' and different concentrations of catalyst [Cat.] (see **Figure 3**) keeping the CO pressure constant and found the linear relationship between [Cat.] and k' (*i.e.* z = 1).

From the above experimental results, we can obtain a kinetic equation as follows:

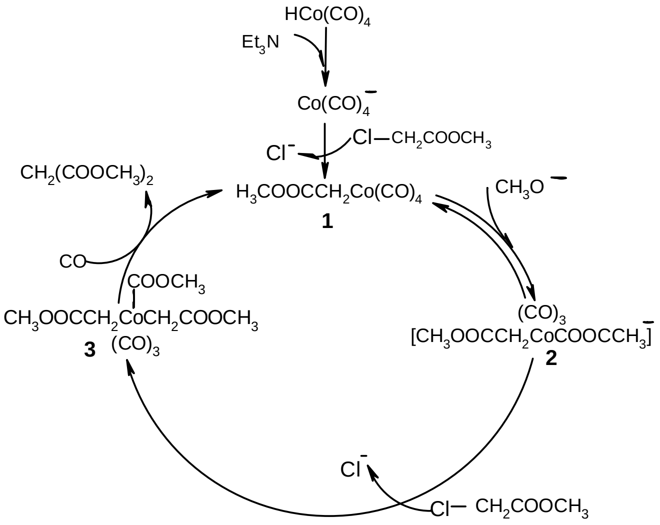
$$r = k\,[Cat.]C$$

**Figure 3** The relationship between rate constant k' and [Cat]



We proposed a reaction mechanism as shown in **Figure 5**. The key step should be the oxidative addition of the methyl chloroacetate to the anionic alkoxycarbonylcobalt complex **2**, leading to a cobalt (III) complex **3**. The reductive elimination of the carbonylation product should regenerate the alkylcobalt carbonyl **1**.

**Figure 5** The scheme of the reaction mechanism



## References

1. Kirk Othmer, Encyclopedia of Chemical Technology, 3rd Edition, John Wiley & Sons, New York, **1981**, Vol. 14, 800-01.
2. T. Kibayashi, K.K. Denki, Pat. Jpn. Kokai Tokkyo Koho ,79, 128,512 05 Oct. **1979**, 3pp.
3. Scheidl F, Pat. Ger. Offen, 2,815,580 25 Oct. **1979**, 11pp.
4. K. K. Denki, Pat. Jpn. Kokai Tokkyo Koho JP, 57,183,741 12 Nov. **1982**, 5pp.
5. K. Watabe, Pat. Jpn. Kokai Tokkyo Koho JP , 63,170,338 14 July **1988**, 4pp.

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