Chinese Chemical Letters Vol. 11, No. 3, pp. 223–224, 2000 223

Cobalt-catalyzed Photochemical Methoxycarbonylation of Olefins with Carbon Dioxide under Ambient Conditions

Jing Mei YIN*[1,] Ming GUO[1,] Rui WANG[1,] Guang Yun ZHOU[1]
Da Bin GAO[2,] Xiang Sheng WANG[2,] Xin Wen GUO[2,] Jian Qin ZHUANG[3]

[1]Department of Chemistry & Chemical Engineering, Dalian University, Dalian, 116622
[2]Open Laboratory of Carbon Resource Utilization, Dalian University of Technology, Dalian,116012
[3]Dalian Institute of Chemical Physics, The Chinese Academy of Sciences, Dalian, 116023

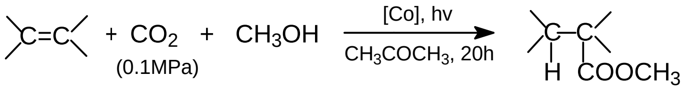
Abstract: The methoxycarbonylations of cyclohexene and 1-decene with CO_2 can take place under ambient conditions by catalysis of [Co]([Co]=Co(acac)$_2$, Co(OAc)$_2$, $CoCl_2$) in the presence of ultraviolet irradiation .

Keywords: Carbon dioxide, methoxycarbonylation, cobalt catalyst .

Carbon dioxide is known to cause harmful greenhouse effect, and what is worse that they are fairly inert . So the way to convert it into more reactive compounds is required . It is known that methoxycarbonylation of olefin is an important basic chemical process, but it is commonly carried out by means of high pressure of CO and temperatures necessary with expensive metal catalysts . From this point of view, it is of great significance to incorporate CO_2 into olefins at ambient conditions[1] . In recent years photocatalyzed carbonylations of CO_2 in place of CO have made advance, for instance, the carbonylation of CO_2 with α,β-unsaturated esters and ketones [2].

Recently we found that CO_2 and olefins in the presence of an alcohol as co-substrate can be converted selectively into corresponding aliphatic esters[3], which was catalyzed by Co(acac)$_2$ under ambient conditions, *i.e.*, under atmospheric pressure of CO_2 at room temperture . This enabled us to study other catalysts and additives for promoting the reaction .

Experimentals and measurement methods are the same as demonstrated in our previous paper[4] . The reaction is as following :



[Co]=Co(acac)$_2$, Co(OAc)$_2$, $CoCl_2$

It was shown that several kinds of cobalt catalysts could catalyze the reaction in different degrees . The results of carbonylation of cyclohexene and 1-decene are shown in **Table 1 .**

Table 1 Effect of [Co]-catalysts on methoxycarbonylation of olefins with carbon dioxide[a]

[Co]	Yield of ester (%)[b]	Yield of ester (%)[c]
Co(acac)$_2$	14	8
Co(OAc)$_2$	13	7
CoCl$_2$	4	2

[a] Olefins 100mmol/L, [Co]10mmol/L, MeOH:CH_3COCH_3=3:1(V:V)(10ml), irradiation of high pressure mercury lamp of 250 watt for 20h, yield and conversion were got by GC analysis, structure were confirmed by GC-MS .

[b] Product of cyclohexene on methoxycarbonylation .

[c] Product of 1-decene on methoxycarbonylation .

It can be seen that catalysis activities are of great difference according to the different anion of cobalt salt . Several kinds of additives such as HOAc, NaOH, Na_3PO_4, Na_2HPO_4, NaH_2PO_4, NaCl, NaOAc and so on, were tried in order to increase the activities of cobalt salt, especially of $CoCl_2$. It was found that weak basic additives promoted the reactions, and NaOAc gave the strongest effect shown in **Table 2 .**

Table 2 Promotion of sodium acetate to methoxycarbonylation of olefins with carbon dioxide catalyzed by [Co][a]

[Co]	Yield of ester (%)[b] ([Co]:NaOAc=mol:mol)[d]	Yield of ester (%)[c] ([Co]:NaOAc=mol:mol)[d]
Co(acac)$_2$	36 (1:40)	22 (1:60)
Co(OAc)$_2$	34 (1:40)	21 (1:60)
CoCl$_2$	25 (1:50)	19 (1:70)

[a] The same as in **Table 1.** [b] The same as in **Table 1.**

[c] The same as in **Table 1.** [d] Optimum ratio is shown in parentheses .

The preliminary explanation of the role of NaOAc, it plays the salt effect, that accelerates the formation of catalytic reactive intermediate and regulates the pH to get optimun reaction media conditions, *i.e.*, weak basicity . It is interesting to find that some amount of CO were formed during reaction by means of GC and IR . Further research are under way to get detailed mechanism .

Acknowledgment

We are indebted to the Natural Science & Technology Foundation Council of Liaoning Province, and Open Laboratory of Carbon Resource Utilization of Dalian University of Technology, for the generous financial support .

References

1. D. Walther, *Coord. Chem., Rev.*, **1987,** *79,* 135.
2. S. Inoue, *J. Am. Chem. Soc.*, **1989,** *111*(8), 3062.
3. J. M. Yin, D. B Gao, M. Guo *et al.*, *Chemistry Online,* **1999**, (13), 99073.
4. D. B Gao, J. M. Yin, M. Guo *et al.*, *Chinese Chem. Lett.*, **1999**, *10*(7), 553.
5. A. Loupy, B. Tchoubar, ‘‘*Salt Effect in Organic and Organometallic Chemistry*’’, New York, VCH Publisher, 1991, p.28.

Received 1 November 1999