APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **14**, 841–843 (2000)

NOTE

Carboxylation of alkali metal phenoxide with carbon dioxide at terrestrial temperature†

Yoshio Kosugi,[1]* Md. A. Rahim,[1] Kazufumi Takahashi,[1] Yoshio Imaoka[2] and Masaya Kitayama[2]
[1]Research Laboratory of Advanced Organic Material Chemistry, Faculty of Science and Engineering, Shimane University, Matsue, Japan 690–8504
[2]Institute for Chemical Science, Ueno Fine Chemicals Industry, Ltd, Techno Park, Sanda City, Hyogo, Japan 669–1339

The reaction between potassium (or sodium) phenoxide and carbon dioxide at room temperature forms salicylic acid and *p*-hydroxybenzoic acid at the same time besides the complex, [alkali metal phenoxide·CO_2]. The complex had been thought an intermediate of the Kolbe–Schmitt reaction but is found inactive to the carboxylation at terrestrial temperatures. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: carbon dioxide; carboxylation of phenoxide

INTRODUCTION

Aspirin, the king of medicine, was commercialized in Germany just 100 years ago. Since then, the Kolbe–Schmitt reaction[1] has been used in the chemical industry. The reaction is important for the production of aromatic hydroxycarboxylic acids. Besides aspirin (acetylsalicylic acid), PAS (*p*-aminosalicylic acid), Paraben (alkyl *p*-hydroxybenzoates) and one of the best engineering plastics (total aromatic liquid crystal polymer) are some of the representative applications of the reaction used today. More than 100 patents for the practical process have appeared to claim better techniques. In the Kolbe–Schmitt reaction, however, the preparation of very hygroscopic alkali phenoxides, the carboxylation with pressurized carbon dioxide at high temperatures (120–300 °C) and normally longer reaction times are required. These adversities make the reaction mechanism ambiguous. In the present study, the carboxylation of phenol has been scrutinized, and a very simple process for the carboxylation with CO_2 has been found.

RESULTS AND DISCUSSION

The CO_2 complex[2] was prepared with a rapid introduction of CO_2 at a pressure of 6.5 MPa over finely powdered potassium phenoxide at room temperature. After work-up with acidification, the resulting white solid was dissolved in dimethylformamide for NMR measurements. The spectra showed unexpected small peaks of salicylic acid (SA) and *p*-hydroxybenzoic acid (pHBA).

There has been no report that the carboxylation occurs in the Kolbe–Schmitt reaction at temperatures as low as room temperature.[3] The yield of the carboxylic acids increased only slightly with prolonged process time, but was affected significantly by the pressure of the CO_2 introduced. The carboxylation did not occur when CO_2 at atmospheric pressure (0.1 MPa) was applied.

The most probable mechanism accepted to date is as follows: the first step of the reaction is the formation of CO_2 complex, [alkali metal phenoxide·CO_2] at temperatures lower than 100 °C. Upon heating of the CO_2 complex, carboxylations at the ortho occur to give such as SA from phenol at 140 °C, *p*-cresotic acid from *p*-cresol at 175 °C, or 3-hydroxy-2-naphthoic acid from naphthol at 240 °C. Further heating of the dipotassium salts of

---

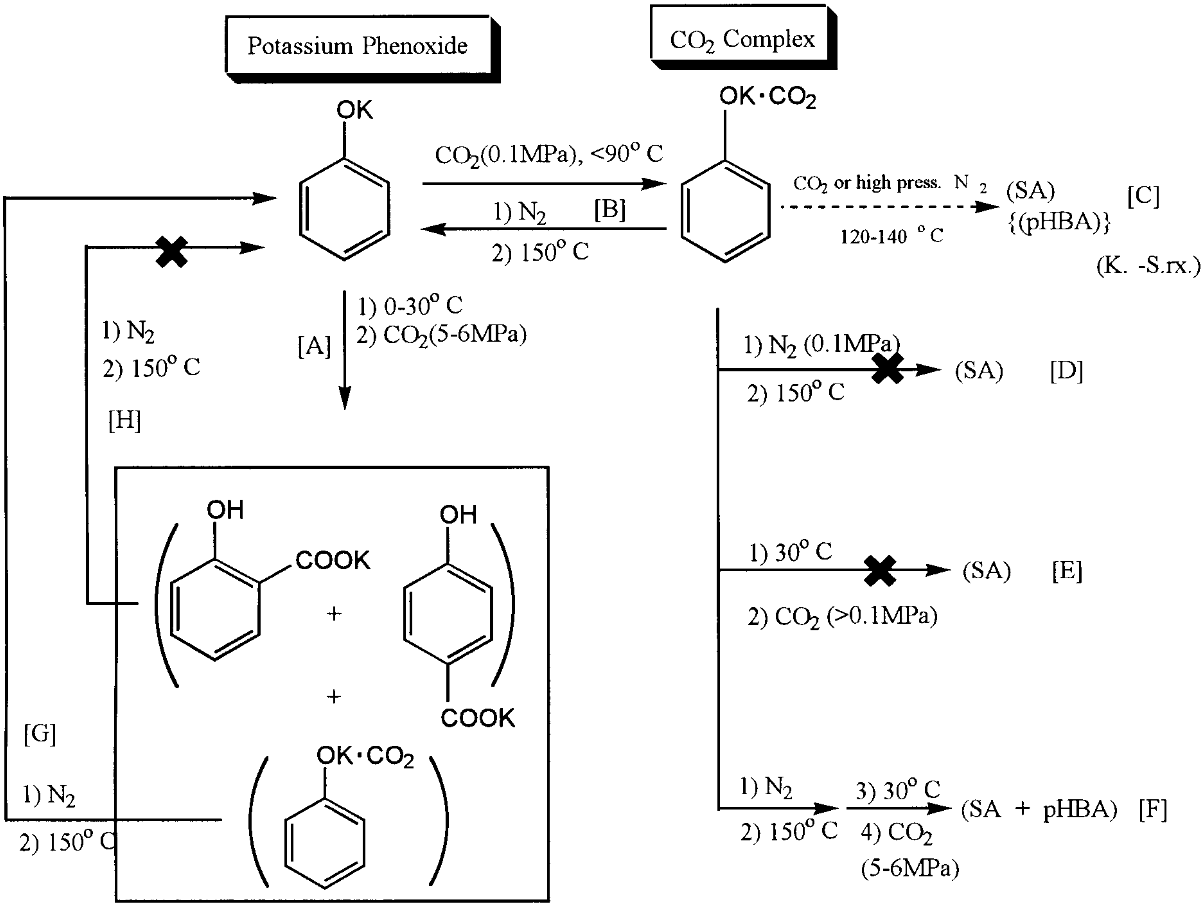
* Correspondence to: Y. Kosugi, Research Laboratory of Advanced Organic Material Chemistry, Faculty of Science and Engineering, Shimane University, Matsue, Japan, 690–8504.
E-mail: kosugi@riko.shimane-u.ac.jp

† This note is based on work presented at the Fifth International Conference on Carbon Dioxide Utilization (ICCDU V), held on 5–10 September 1999 at Karlsruhe, Germany.

Table 1 Carboxylation of potassium phenoxide at 30 °C

Run no.	CO_2 pressure (MPa)	Reaction time (min)	Yield (%) of carboxylic acids		
			SA	pHBA	Total
1	6.5	0	7.9	5.1	13.0
2	6.5	0.5	6.6	4.4	11.0
3	6.5	1	9.3	5.9	15.2
4	6.5	10	8.8	6.5	15.3
5	0.1	10	0.0	0.0	0.0
6	1.0	10	4.5	2.6	7.1
7	4.0	10	6.7	4.1	10.8
8	7.2	10	11.4	7.2	18.6
9 (complex)[a]	6.5	60	0.0	0.0	0.0
10 (complex)[a]	6.5	10	0.0	0.0	0.0

[a] [Potassium phenoxide·CO_2] complex instead of potassium phenoxide was used.



Scheme 1.

Table 2 Repeated carboxylations at terrestrial temperature

Run no.	Substrate	CO_2 (MPa)	Reaction temp. (°C)	Carboxylation (no. of times)	Decomposition		Yield (%)		
					Temp. (°C)	No. of times	SA	pHBA	Total
11	PhOK	6.9	30	1	—	0	11.4	6.4	17.8
12	PhOK	7.2	60	2	150	1	22.0	16.9	38.9
13	PhOK	7.1	30	3	150	2	28.4	19.2	47.6
14	PhONa	5.2	30	1	—	0	17.7	2.7	20.4
15	PhONa	5.4	30	2	150	1	35.1	4.0	39.1
16	Complex[a]	7.2	30	1	150	1	8.4	7.0	15.4

[a] [Potassium phenoxide·CO_2] complex instead of potassium phenoxide was used, and decomposed in N_2 first, then the carboxylation was conducted for 10 min.

the ortho-carboxylated phenols causes rearrangement to the corresponding *para*-carboxylic acids such as pHBA from SA,[4] and 6-hydroxy-2-naphthoic acid from 3-hydroxy-2-naphthoic acid.[1c]

Contrary to these known mechanisms, the present results indicate that the carboxylation is very fast even at room temperature and is competitive with the formation of the CO_2 complex. A slow introduction of CO_2 of a lower pressure is favorable to the formation of the CO_2 complex. Thus ‘pure CO_2 complex’ was prepared with CO_2 of 0.1 MPa. When this complex was subjected to CO_2 of a high pressure (6.5 MPa) for a longer time (10–60 min) at 30 °C, only phenol was recovered in 100% after work-up (run nos 9 and 10 in Table 1). This fact clearly shows the complex is not an intermediate of the carboxylation reaction.

The direct carboxylation, is not via the complex, occurs on the *ortho* and *para* positions of phenoxide with the attack of CO_2, which is probably activated with alkali metal ion in the system. On the other hand, the coordination of alkali metal ions to the CO_2 molecule in the complex makes the aromatic ring less nucleophilic towards the reactive CO_2. This assumption is further confirmed by the following experiments.

Once the CO_2 complex forms, the carboxylation does not proceed further. Therefore, the complex was decomposed to phenoxide by heating at 150 °C under nitrogen atmosphere. Then CO_2 of a high pressure was introduced to the cooled mixture in the autoclave. The competitive reactions between carboxylation and reformation of the complex started again. The yield of carboxylic acids was doubled after the second carboxylation, and almost tripled with another repetition of the combination process of decomposition–carboxylation. This method can be applied not only to potassium or sodium phenoxide but also to ‘pure CO_2 complex’ (see run no. 16 in Table 2). The present results are summarized in Scheme 1.

EXPERIMENTAL

Potassium and sodium phenoxides were prepared with phenol and the corresponding metal hydroxides. Then 2.5g of the prepared fine powdered phenoxide was placed in a 200 ml autoclave, and purged with N_2 gas prior to the introduction of CO_2. The reaction mixture was acidified and analyzed by high performance liquid chromatography. In the repetitive carboxylation, the CO_2 pressure was released and N_2 gas was used to fill up the reactor, which was then heated at 150 °C for 1 hr. After the decomposition, the autoclave was cooled for the next carboxylation.

REFERENCES

1. (a) Kolbe H, Lautemann E. *Ann.* 1860; **115**: 178. (b) Schmitt R. *J. Prakt. Chem. [2]* 1885; **31**: 397. (c) Lindsey AS, Feskey H. *Chem. Rev.* 1957; **57**: 583.
2. (a) Hales JL, Jones JI, Lindsey AS. *J. Chem. Soc.* 1954; 3145. (b) Dewar MSJ. *The Electronic Theory of Organic Chemistry*, Oxford University Press: London, 1949; 168–171.
3. (a) Hirao I, Kosugi Y, Kito T. *Yuuki Gosei Kagaku Kyoukai Shi (J. Synth. Org. Chem. Jpn.)* 1968; **26**: 439 (in Japanese); (b) Hirao, I, Kosugi, Y, Matsuura T, Hironaka Y. *Yuuki Gosei Kagaku Kyoukai Shi (J. Synth. Org. Chem. Jpn.)* 1967; **5**: 417. (c) Kwan T, Yamamoto H, Mori H, Samejima H. *Kagaku Kogyo (Chem. Ind.)*, 1972; (12) 618 (in Japanese).
4. (a) Ueno R. *Kagaku to Kogyo (Sci. Ind.)* 1959; **33**: 317 (in Japanese). (b) Ueno R. *Kogyo Kagaku Zasshi (J. Ind. Chem.)* 1960; **60**: 517 (in Japanese).