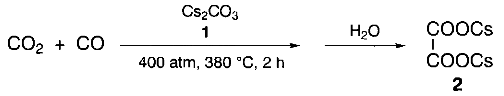
Novel Synthesis of Oxalate from Carbon Dioxide and Carbon Monoxide in the Presence of Caesium Carbonate

Kiyoshi Kudo,* Futoshi Ikoma, Sadayuki Mori, Koichi Komatsu and Nobuyuki Sugita
Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, Japan
E-mail:komatsu@scl.kyoto-u-ac.jp

In the presence of caesium carbonate **1**, the direct reaction of CO_2 (110 atm) with CO (20 atm) results in reductive capture of CO_2 to give caesium oxalate **2** in good yield at elevated temperature (380 °C).

There is a great deal of current interest in the chemistry of CO_2, aimed in particular at new catalytic processes for the conversion of abundant CO_2 into organic chemicals of commercial value.[1] As far as the reductive transformation of CO_2 is concerned, various methods have been developed,[2] amongst which, the catalytic reduction of CO_2 with H_2 seems to be an effective method.[3] In homogeneous catalysis in solution, the reaction between CO_2, H_2 and alcohols or amines (R_2NH) lead to formates[4] or formamides.[5]

Here, we report the novel formation of a carbon–carbon bond *via* coupling of CO_2 and CO in the presence of Cs_2CO_3 **1**, which gives caesium oxalate **2** in high yield after hydrolysis [eqn. (1)].



$$CO_2 + CO \xrightarrow[400\ \text{atm},\ 380\ ^\circ\text{C},\ 2\ \text{h}]{Cs_2CO_3\ \mathbf{1}} \xrightarrow{H_2O} \underset{\mathbf{2}}{\begin{matrix}COOCs\\ |\\ COOCs\end{matrix}} \qquad (1)$$

It is well known that pyrolysis of alkali metal formates yields the corresponding oxalates. However, there has been no study reported on the reductive capture of CO_2 with CO to form oxalate **2**. This transformation is unique in that it suggests a rare example of an intermediate formation of adduct complex [$\mathbf{1}\cdot CO_2$] **3** and represents a totally new mode of reductive capture of CO_2 with CO.

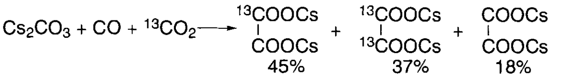
Representative results are summarized in Table 1.† For example, the reaction of CO_2 (110 atm) with CO (20 atm) in the heterogeneous system including **1**(4.5 mmol) afforded **2** in 22.4% yield (based on charged **1** at 29.4% conversion of **1**), along with $CsHCO_3$ (13.0%) and HCO_2Cs (2.1%) after hydrolysis (entry 4). As is apparent from the results of entries 1–3, the present reaction is characteristic of the caesium salt **1**. The difference in reactivity among the carbonate salts is ascribed to the differing sizes of the alkali metal ions. The caesium ion is particularly large and is anticipated to be only weakly paired with the counter-anion of the carbonate. This would presumably facilitate the coordination of CO_2 to the caesium carbonate compared with the other alkali metal carbonates. Under the best conditions, **2** was obtained in 90.1% (entry 5).

The combination of CO and CO_2 is essential for the formation of **2**, *i.e.* the reaction did not proceed at all without CO (entry 6), and only a low yield of **2** was obtained from the reaction with CO alone (entry 7). The yield of **2** was significantly affected by the partial pressure of CO (entries 4 and 5).

When dry **1** was kept in contact only with CO_2, 21.3% of **1** was consumed and $CsHCO_3$ was produced in about twice the amount (39.2%) of consumed **1** upon hydrolysis of the resulting solid product (entry 6). This solid product also evolved CO_2 in an amount (19.6%) nearly equivalent to that of consumed **1** when heated again at 380 °C for 1 h under an argon atmosphere. Furthermore, the solid product formed from **1** and CO_2 (200 atm) at 380 °C for 1 h exhibited a new strong IR absorption at 1660 cm^{-1} which is characteristic of CO_2 complexed with an alkali metal compound.[6] These facts suggest the intermediate formation of complex **3**, which decomposes to 2 equiv. of $CsHCO_3$ after hydrolysis, as shown in Scheme 1.

In support of the formation of complex **3**, oxalate **2** was obtained in 16% yield when the solid product formed under the conditions of entry 6 was treated with CO (50 atm) at 380 °C for 1 h. In contrast, a reaction conducted in reverse order, *i.e.* the reaction of the solid product of entry 7 with CO_2 (100 atm) gave **2** in only 4% yield under similar conditions.

In order to examine the origin of the carbonyl carbon in **2**, ^{13}C-labelling experiments were conducted and the products analysed with GC–MS.‡ When the reaction was carried out using ^{13}C-labelled CO_2 and non-labelled CO (20 atm, total pressure 150 atm) at 380 °C for 2 h, the ^{13}C was incorporated in the produced oxalate as shown in eqn. (2). In addition,



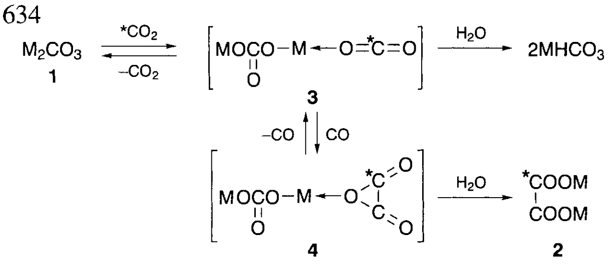
$$Cs_2CO_3 + CO + {}^{13}CO_2 \longrightarrow \underset{45\%}{\begin{matrix}{}^{13}COOCs\\ |\\ COOCs\end{matrix}} + \underset{37\%}{\begin{matrix}{}^{13}COOCs\\ |\\ {}^{13}COOCs\end{matrix}} + \underset{18\%}{\begin{matrix}COOCs\\ |\\ COOCs\end{matrix}} \qquad (2)$$

considerable amounts of ^{13}C-labelled CO ($^{13}CO:CO$ = 1 : 1) and non-labelled CO_2 ($^{12}CO_2:{}^{13}CO_2$ = 1 : 2.7) were observed in the resulting gaseous mixture. On the contrary, no ^{13}C was found in the oxalate when ^{13}C-labelled **1** ($Cs_2{}^{13}CO_3$) and non-labelled CO_2 were employed. These results clearly indicate that the carbonyl carbon atom of **2** is derived from external CO_2 and CO gases, and a rapid scrambling of ^{13}C takes place between CO and CO_2.

Table 1 Caesium carbonate-mediated synthesis of oxalate from CO and CO_2[a]

Entry	M in M_2CO_3	CO/atm	CO_2/atm	Conv (%)[b]	Yields (%)[c] 2	MHCO$_3$	HCO$_2$M
1	Na	20	110	1.0	0	0.5	0
2	K	20	110	1.0	Trace	0.8	0
3	Rb	20	110	13.6	2.2	17.2	6.9
4	Cs	20	110	29.4	22.4	13.0	2.1
5	Cs	50	110	97.5	90.1	0.1	7.7
6	Cs	0	400	21.3	0	39.2	0
7	Cs	80	0	4.5	4.4	0	6.9

[a] Carried out with various carbonates (M_2CO_3 = 4.5 mmol) at 380 °C for 2 h. Other conditions as described in Footnote†. [b] Conversion of M_2CO_3 based on the charged amount of M_2CO_3. [c] Based on the charged M_2CO_3; **2** and formate were determined by HPLC (Shimadzu LC-10A, Shim-pack SCR-101H column), and M_2CO_3 and $MHCO_3$ were determined by titration with 0.1 mol dm^{-3} HCl according to the method described in ref. 7.



Scheme 1 M = Cs

We propose that the reaction proceeds through the intermediary of the complex **3** and **4** as shown in Scheme 1; *i.e.* the first-formed complex **3** is subjected to nucleophilic attack of CO at the activated CO_2 to form the second complex **4**, in which two carbonyl carbons make a quasi-three-membered ring. This complex can be formally considered to contain a structure of oxalic anhydride, and would be readily hydrolysed to give the oxalate **2** (Scheme 1). Thus, caesium carbonate **1** operates not only as an effective CO_2 activator, but also as a base that stabilizes the oxalate precursor **4**.

In conclusion, this novel synthesis of oxalate represents an intriguing reductive coupling reaction of CO_2 with CO by the use of the readily available alkali metal carbonate.

Received, 4th November 1994; Com. 4/06756H

Footnotes

† A typical procedure is as follows. Powdered **1** (4.5 mmol) was charged into a Pyrex-glass lined shaking-type autoclave (*ca.* 20 ml) and was dried under vacuum at 120 °C for 1 h. After cooling to room temp., liquid CO_2 (0.28 mol) and CO (20 atm) were charged into the autoclave, and the mixture heated and shaken constantly at 380 °C for 2 h. After cooling, the reaction mixture was dissolved into water (50 ml), acidified with dilute perchloric acid, and then analysed by HPLC.

‡ ^{13}C-Labelled caesium carbonate (99 atom% ^{13}C) and CO_2 (99 atom% ^{13}C) were purchased from MSD Isotopes, France. These reactions were carried out similarly by the use of a 5 ml autoclave.

References

1 *Organic and Bioorganic Chemistry of Carbon Dioxide*, ed. S. Inoue and N. Yamazaki, Wiley, New York, 1982.

2 B. A. Parkinson and P. E. Weaver, *Nature*, 1984, **309**, 148; Y.Hori, A. Murata, R. Takahashi and S. Suzuki, *J. Am. Chem. Soc*, 1987, **109**, 5022; H. Ishida, K. Tanaka and T. Tanaka, *Organometallics*, 1987, **6**, 181; G. D. Weatherbee and C. H. Bartholomew, *J. Catal.*, 1984, **87**, 352.

3 E. Graf and W. Leitner, *J. Chem. Soc., Chem. Commun.*, 1992, 623; F. Gassner and W. Leitner, *J. Chem. Soc., Chem. Commun.*, 1993, 1465; P. G. Jessop, T. Ikariya and R. Noyori, *Nature*, 1994, **368**, 232.

4 D. J. Darensbourg and C. Ovalles, *J. Am. Chem. Soc.*, 1987, **109**, 3330, and references cited therein.

5 P. Haynes, L. H. Slaugh and J. F. Kohnle, *Tetrahedron Lett.*, 1970, 365; K. Kudo, H. Phala, N. Sugita and Y. Takezaki, *Chem. Lett.*, 1977, 1495; H. Phala, K. Kudo and N. Sugita, *Bull. Inst. Chem. Res., Kyoto Univ.*, 1981, **59**, 88.

6 J. l. Hales, J. Idris Jones and A. S. Lindsey, *J. Chem. Soc.*, 1954, 3145; I. Hirao and T. Kito, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 3470.

7 C. Winker, in F. P. Treadwell and W. T. Hall, *Analytical Chemistry*, 6th edn., Wiley, New York, 1924, vol. 2, pp. 485–487.