Synthesis of oxalate from carbon monoxide and carbon dioxide in the presence of caesium carbonate

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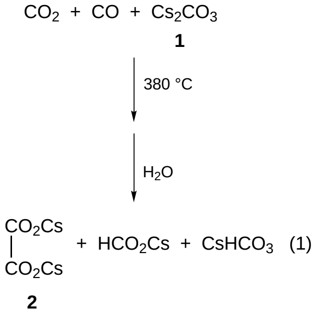
In the presence of caesium carbonate, the direct reaction of CO_2 (110 atm) with CO (50 atm) resulted in reductive capture of CO_2 to give caesium oxalate in good yield (90.1%) at high temperature (380 °C). The reaction is characteristic of caesium carbonate. When lithium, sodium, potassium and rubidium carbonates were used, oxalate was scarcely produced. The effects of the reaction variables, such as the pressures of CO_2 and CO, and the reaction temperature, were examined to optimize the process. From the results of mechanistic studies including a separately examined two-step reaction, ^{13}C-labelling experiments and IR spectroscopic studies of the intermediates, it was concluded that the reaction proceeds through a nucleophilic addition of CO upon the carbonyl carbon of CO_2 which is activated by the complexation to caesium carbonate.

Introduction

Needless to say, the efficient utilization of abundant CO_2 on earth is one of the most important current issues not only from the interest in its chemistry but from the standpoint of environmental protection. As far as the reductive transformation of CO_2 is concerned, various methods have been developed.[1] Among them, the catalytic reduction of CO_2 with H_2 seems to be an effective method.[2] In homogeneous catalysis in solution, the reaction of CO_2 and H_2 with alcohols or secondary amines leads to formates[3] or formamides.[4] Particularly noteworthy is the recent work by Noyori and co-workers on an efficient hydrogenation of CO_2 in the supercritical phase.[5]

In the course of our studies on the pyrolysis of alkali metal formate in supercritical CO_2, we found a novel reaction of CO and CO_2 in the presence of caesium carbonate (**1**), which gives caesium oxalate (**2**) in high yield after hydrolysis of the resulting solid product [eqn. (1)].[6] Although the oxalate **2** can be synthesized by the pyrolysis of alkali metal formates,[7] a direct synthesis of **2** *via* the reductive capture of CO_2 with CO is very attractive.



$$CO_2 + CO + \underset{\mathbf{1}}{Cs_2CO_3} \xrightarrow{380\ °C} \xrightarrow{H_2O} \underset{\mathbf{2}}{\begin{array}{c}CO_2Cs\\ |\\ CO_2Cs\end{array}} + HCO_2Cs + CsHCO_3 \quad (1)$$

In this paper, we report full details concerning the novel formation of a carbon–carbon bond, which is one of the most fundamental reactions in organic synthesis, *via* the coupling of two simple and basic inorganic compounds, CO and CO_2.

Results and discussion

Effects of the reaction variable

When caesium carbonate **1** (4.5 mmol) was heated at 380 °C under pressurized CO (20 atm) and CO_2 (110 atm) in an autoclave for 2 h, oxalate **2** was obtained in 22.4% yield (based on the initial amount of **1**) together with smaller amount of caesium hydrogen carbonate ($CsHCO_3$) (13%) and caesium formate (HCO_2Cs) (2.1%) after aqueous work-up. This reaction proceeds as a solid–gas heterogeneous system in supercritical CO_2. We also compared the reactivities of other alkali metal carbonates; the results are shown in Table 1. As is apparent from Table 1, the present reaction is characteristic of caesium carbonate **1**. Carbonates of other alkali metals, such as lithium, sodium, potassium and rubidium, showed quite low or almost no reactivity to give oxalate (Runs 1–4). The difference in reactivity among the carbonate salts is ascribed to the differing sizes of the alkali metal ions. The caesium ion, which has the largest ionic radius, 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 carbonate.

Table 1 Synthesis of oxalate from CO and CO_2[a]

Run	M_2CO_3 M	Conv. (%)[b]	Yields (%)[b] $(CO_2M)_2$	$MHCO_3$	HCO_2M
1	Li	1.0	0	0.5	0
2	Na	1.0	0	0.5	0
3	K	1.0	Trace	0.8	0
4	Rb	13.6	2.2	17.2	6.9
5	Cs	29.4	22.4	13.0	2.1

[a] Conditions: M_2CO_3 (**1**) (4.5 mmol), CO (20 atm at room temp.), CO_2 (110 atm at 380 °C), 380 °C, 2 h. [b] Based on the charged M_2CO_3. Oxalate **2** and formate were determined by HPLC and M_2CO_3 and $MHCO_3$ were determined by titration with 0.1 mol dm^{-3} HCl.

Next, in order to determine the optimum reaction conditions, the effect of the reaction temperature on the yield and products distribution was examined under pressurized CO (20 atm) and CO_2 (110 atm) to give the results shown in Fig. 1. The highest yield of the product **2** was achieved at 380 °C and then decreased at higher temperature. Decreasing the temperature to 320 °C greatly retarded the reaction, and the amount of $CsHCO_3$ increased. Higher temperature (>400 °C) did not offer any advantages. The yield of HCO_2Cs was very low and gradually decreased with an increase in the reaction temperature.

The effects of partial pressures of both CO_2 and CO on the reactivity of **1** at 380 °C are shown in Table 2. Compound **2** was not formed at all from CO_2 only (Runs 1 and 2), and the yield of

Table 2 Effects of partial pressures of CO and CO_2[a]

Run	p(CO)[b]/ atm	$p(CO_2)$[c]/ atm	Conv. and yields(%)[d] Conv.	$(CO_2Cs)_2$ (**2**)	$CsHCO_3$	HCO_2Cs
1	0	110	6.0	0	12.0	0
2	0	400	21.3	0	39.2	0
3	20	0	2.5	1.4	0	3.6
4	50	0	7.5	5.6	0	7.8
5	80	0	4.5	4.4	0	6.8
6	20	110	29.4	22.4	13.2	2.1
7	20	190	40.0	29.1	12.3	1.6
8	20	310	61.5	40.0	36.8	1.5
9	20	360	66.0	48.0	42.6	1.3
10	20	565	91.3	74.0	21.0	1.1
11	10	110	18.5	12.1	12.5	1.1
12	35	110	56.2	46.3	8.1	4.5
13	50	110	97.4	90.1	0.1	7.7

[a] Conditions: **1** (4.5 mmol), 380 °C, 2 h. [b] Partial pressure of CO at room temp. [c] Partial pressure of CO_2 at 380 °C. [d] Based on the charged carbonate **1**.

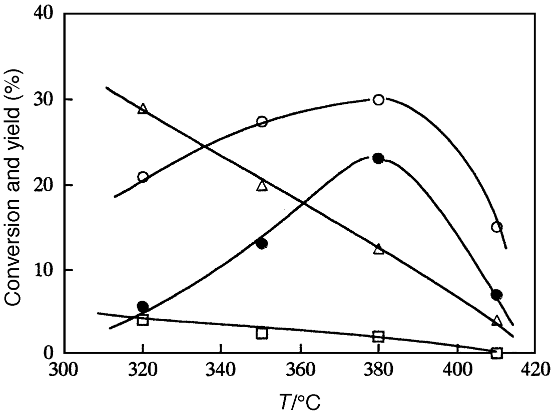


Fig. 1 Effect of reaction temperature on the conversion and product yields. Conditions: **1** (4.5 mmol), CO (20 atm), CO_2 (110 atm); reaction time, 2 h. ○: conversion of **1**, ●: yield of **2**, △: yield of $CsHCO_3$, □: yield of HCO_2Cs.

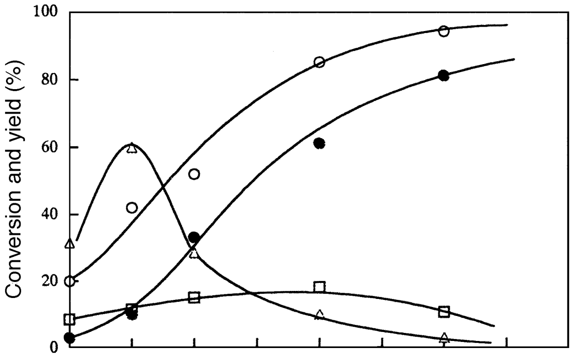


Fig. 2 Effect of reaction time on the conversion and product yields. Conditions: **1** (4.5 mmol), CO (50 atm), CO_2 (110 atm), 380 °C. ○: conversion of **1**, ●: yield of **2**, △: yield of $CsHCO_3$, □: yield of HCO_2Cs.

2 was only minute from the reaction with CO alone (Runs 3–5). Therefore, the combination of CO and CO_2 appears to be essential for the formation of **2**. This result suggests that the carbon content in the product **2** is derived from both CO_2 and CO. The conversion of **1** and yield of **2** increased with increasing partial pressures of CO_2 or CO (Runs 6–10). The effect of CO pressure was much greater than that of CO_2 pressure, *i.e.* by increasing the CO pressure from 10 to 50 atm the yield of **2** increased from 12.1 to 90.1% (Runs 11–13). It should be noted that when **1** was heated under CO_2 pressure, $CsHCO_3$ was produced in about twice the amount of **1** consumed upon hydrolysis of the resulting solid product (*vide infra*) (Runs 1 and 2).

The yield–time profile of the products in the reaction of CO_2 (110 atm) with CO (20 atm) in the presence of **1** is shown in Fig. 2. At an early stage (*ca.* 10 min), the yield of $CsHCO_3$ reached a maximum value, then decreased and was finally replaced by **2**. This reaction was complete within *ca.* 60 min, and afforded **2** in 81% along with a small amount of HCO_2Cs (6%). As will be discussed below, the presence of a maximum in the yield of $CsHCO_3$ is of interest in connection with an activation step of CO_2. Here, it is assumed that CO_2 would first interact with **1** to give adduct complex **3**, which would be easily converted to $CsHCO_3$ upon hydrolysis [eqn. (2)]. Further reaction of complex **3** with CO can lead to the formation of the second complex **4**, which can be a direct precursor to **2** [eqn. (3)]. Under the present reaction conditions, both the formation of **3** and its transformation to **4** are assumed to be reversible, and the carbonate **1** is assumed to act as a base to capture CO_2 in the first step [eqn. (2)] and provide itself as a medium for the reaction of CO with the activated CO_2 in the second step [eqn. (3)].

$$\mathrm{CO_2 + \underset{\mathbf{1}}{Cs_2CO_3} \rightleftharpoons \underset{\mathbf{3}}{[Cs_2CO_3{\cdot}CO_2]} \xrightarrow{H_2O} 2CsHCO_3} \quad (2)$$

$$\mathrm{\underset{\mathbf{3}}{[Cs_2CO_3{\cdot}CO_2]} + CO \rightleftharpoons \underset{\mathbf{4}}{[Cs_2CO_3{\cdot}CO_2{\cdot}CO]} \xrightarrow{H_2O} \underset{\mathbf{2}}{(CO_2Cs)_2}} \quad (3)$$

Mechanistic studies

In order to verify the above assumption of the two-step reaction, each of the two reactions of eqns. (2) and (3) was examined separately, *i.e.* the reaction of **1** with CO_2 (100 atm) was carried out for 1 h as the first step and then, after the CO_2 gas in the autoclave had been replaced completely by CO at room temperature, the reaction mixture was again heated under CO pressure (75 atm) for 1 h as the second step at various temperatures. The effects of the temperature of each step on the yield of **2** are shown in Table 3. Each reaction step has a different optimum temperature. The first step required relatively lower temperatures (*ca.* 200 °C) for the optimum yield of **2**, while the second step gave a higher yield of **2** at a temperature of *ca.* 380 °C (Runs 5–7). Thus, as was shown in Fig. 1, the yield of **2** increased with temperature in reverse to that of $CsHCO_3$, but the maximum yield of **2** was obtained at *ca.* 380 °C. The results of Table 3 show that the first-step reaction at 200 °C followed by the second-step reaction at 380 °C gives the highest yield of **2** (Run 2). Furthermore, it should be noted that a reaction conducted in the reverse order, *i.e.* the reaction of **1** with CO prior to that with CO_2 gave **2** only in 4% yield at 380 °C (Run 8).

In the Kolbe-Schmidt reaction, it is known that an addition complex $[PhOM{\cdot}CO_2]$ is formed when alkali metal phenoxide (PhOM) comes into contact with CO_2, and this complex is very sensitive to heat.[8] Owing to the similarity between this and the first-step [eqn. (2)], we also examined the effect of the temperature on the reaction of **1** with CO_2 by the determination of $CsHCO_3$ obtained after aqueous work-up, and the results are shown in Fig. 3. As might be expected from Table 3, the maximum in both the conversion of **1** and yield of $CsHCO_3$ was observed at *ca.* 200 °C. Here, it should be noted that the amount of $CsHCO_3$ obtained was always about twice that of the conversion of **1**. After the same procedure, K_2CO_3 gave only 1.2% of $KHCO_3$ and K_2CO_3 was 96.5% recovered under 400 atm of CO_2 at 200 °C for 1 h. In support of the formation of complex

Table 3 Effect of reaction temperatures on the two-step reaction[a]

Cs_2CO_3	$\xrightarrow{CO_2\ 100\ atm}$	$\xrightarrow{CO\ 75\ atm}$	$\xrightarrow{H_2O}$ $(CO_2Cs)_2$
1	Step 1 (1 h)	Step 2 (1 h)	**2**
Run	Temp. of step 1/ °C	Temp. of step 2/ °C	Yield of **2**(%)[b]
1	150	380	25
2	200	380	56
3	260	380	23
4	320	380	20
5	380	380	16
6	380	350	7
7	380	410	5
8[c]	380	380	4

[a] Conditions: **1** (4.5 mmol). Step 1 reaction was followed by step 2 reaction after CO_2 gas was released from the reaction mixture at room temp. [b] Based on the charged **1**. [c] In the reversed order reaction.

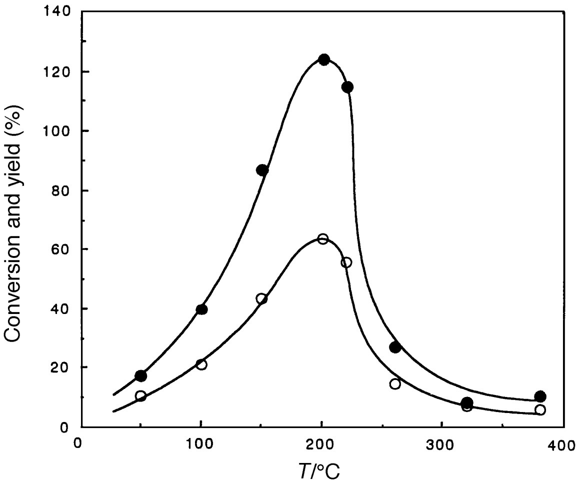


Fig. 3 Effect of the reaction temperature on the formation of complex **3**. Conditions: **1** (4.5 mmol), CO_2 (110 atm), 1 h. ●: yield of $CsHCO_3$, ○: conversion of **1**.

3, when the resulting solid product of Run 2 in Table 2 was heated at 380 °C for 1 h under argon atmosphere, CO_2 was evolved in an amount nearly equivalent (19.6%) to that of **1** consumed (21.3%), and **1** was 97.5% recovered.

On the basis of the above results, it can be said that the CO_2 binds loosely to the caesium atom of **1**, complex **3** in Scheme 1 (see later). Therefore, this complex **3** readily decomposes into its components under low pressures on heating. The formation of $CsHCO_3$ from the complex **3** on aqueous work-up probably arises from its decomposition into **1** and CO_2, which is subsequently absorbed by the aqueous solution of **1** to give 2 equiv. of $CsHCO_3$ as follows: $Cs_2CO_3 + CO_2 + H_2O \longrightarrow 2CsHCO_3$.

Alkali metal phenoxide–CO_2 complexes have been discussed because they have been regarded by some investigators as important intermediates in the carboxylation of alkali phenoxides, *i.e.*, the Kolbe–Schmidt reaction. Based on an IR study, Hales *et al.* determined the structure of the complex obtained from sodium phenoxide and CO_2.[8a] They proposed that CO_2 in the complex is bent and its oxygen atom binds to the alkali atom.

Fig. 4 shows the IR spectra of the solid products, which were obtained from the reaction of **1** with CO_2 (160 atm) for 2 h at 200 and 380 °C, respectively, together with the spectrum of starting compound **1** for comparison. The spectrum of the product obtained at 200 °C [Fig. 4(*a*)] shows a strong absorption near 1650 cm^{-1}, which is assignable to a carbonyl stretching ν(C=O) and is diagnostic of CO_2 complexed with an alkali metal compound,[8] with two characteristic absorptions of the carbonate **1** (1380 and 1450 cm^{-1}) merged into one peak. This material did not show any significant change for several days at room temperature. In contrast, the product obtained at 380 °C [Fig. 4(*b*)] shows a considerable decrease in the absorption at *ca.* 1650 cm^{-1} accompanied by the reappearance of the absorptions in both the 1380 and 1450 cm^{-1} regions, resembling **1** [Fig. 4(*c*)]. These data are in agreement with the results of Table 3 and Fig. 3, indicating that the formation of complex **3** is highly sensitive to temperature and unfavourable at higher temperatures.

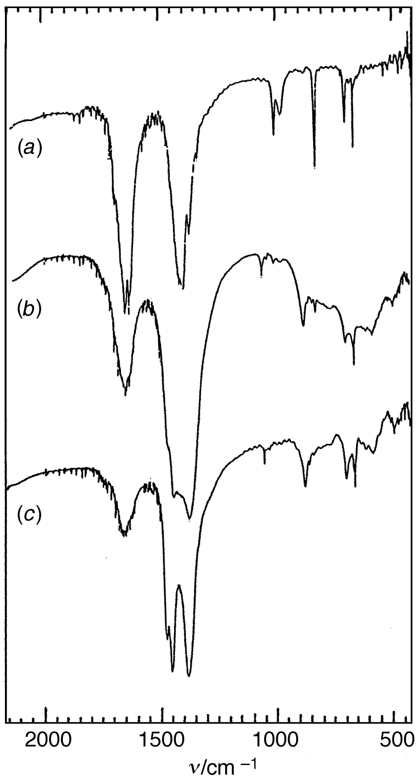
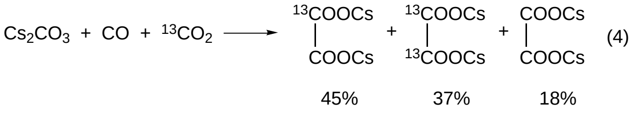


Fig. 4 IR spectral change of Cs_2CO_3 after reaction with CO_2 (160 atm): (*a*) at 200 °C for 2 h, (*b*) at 380 °C for 2 h, (*c*) IR spectrum of Cs_2CO_3

In order to elucidate the origin of the carbonyl carbon in the product **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. (4). In addition,

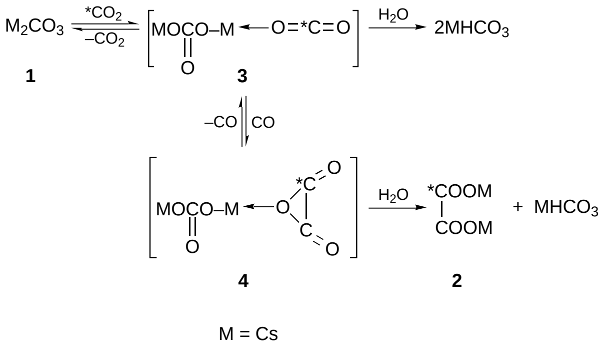


$$Cs_2CO_3 + CO + {}^{13}CO_2 \longrightarrow \begin{array}{c} {}^{13}COOCs \\ | \\ COOCs \\ 45\% \end{array} + \begin{array}{c} {}^{13}COOCs \\ | \\ {}^{13}COOCs \\ 37\% \end{array} + \begin{array}{c} COOCs \\ | \\ COOCs \\ 18\% \end{array} \quad (4)$$

considerable amounts of ^{13}C-labelled CO ($^{13}CO : CO = 1:1$) and non-labelled CO_2 ($CO_2 : {}^{13}CO_2 = 1:2.7$) were observed in the resulting gaseous mixture. In contrast, 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. Clearly, these results indicate that the carbonyl carbon of the product **2** is derived from external CO_2 and CO gases, and a rapid scrambling of ^{13}C takes place between CO and CO_2.

Based on these results, 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 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, it has been shown that the readily available



Scheme 1

alkali metal carbonate Cs_2CO_3 can act as an effective CO_2-trapping activator, for an intriguing reductive coupling reaction of CO_2 with CO to give an organic carbon compound, oxalate.

Experimental

Materials

Alkali metal carbonates were obtained commercially, and were further dried by heating (at 180 °C) under reduced pressure before use. ^{13}C-Labelled caesium carbonate (99 atom% ^{13}C) and CO_2 (99 atom% ^{13}C) were obtained from MSD Isotopes in France. Carbon dioxide and CO were commercially supplied by Kyoto Teisan, Inc. and used without further purification.

Measurements

The HPLC analysis was carried out on a Shimadzu LC-10A using a column packed with SCR-101H (25 cm × 6 mm) eluted with aqueous perchloric acid (pH 2.1) solution. The peak areas were determined by using a Shimadzu chromatopac C-R6A integrator. The GC–MS analysis for the products of ^{13}C-labelled experiments was performed on a Nichiden-Varian NEVA-TE600 spectrometer using a column packed with PEG-HT for oxalate (as methyl ester) or a column packed with Active Carbon for CO and CO_2 gases. The IR spectra of the solid products obtained from the reaction of **1** with CO_2 or the reaction of **1** with CO_2–CO were recorded on a Shimadzu FTIR-8600 spectrometer for their samples as KBr pellets. Each spectrum was obtained 12–24 h after taking out from the autoclave. The contents of alkali metal carbonate and alkali metal hydrogencarbonate in the aqueous solution were determined by the classical titration method with 0.1 M HCl, using phenolphthalein and methyl orange as an indicator.

General procedure

Single-step reaction. A typical procedure is as follows. A Pyrex-glass test tube, in which 1.46 g (4.5 mmol) of powdered **1** had been placed, was inserted into a shaking-type autoclave (*ca.* 20 ml) and was dried under vacuum at 120 °C for 1 h. After cooling to room temperature, liquid CO_2 (12.5 g) and CO (20 atm) were charged into the autoclave, and the mixture heated and shaken constantly at 380 °C for 2 h. After the autoclave had been rapidly cooled by air-blowing, the reaction gases were purged. The reacted carbonate was left as a partly molten solid. The reaction mixture was dissolved in water (50 ml), acidified with dilute (pH 2.1) perchloric acid, and then oxalate and formate were analysed by HPLC. The reactions using ^{13}C-labelled **1** or CO_2 were carried out similarly by the use of a 5 ml autoclave.

Two-step reaction. A typical procedure for the two-step reaction is as follows. First, **1** (4.5 mmol) was charged in the autoclave and heated at 200 °C under CO_2 pressure (160 atm). After 1 h, it was allowed to cool to room temperature, the pressure was released and then CO_2 was thoroughly replaced by CO (20 atm). After *ca.* 30 min, the autoclave was again heated at 380 °C for 1 h. The work-up and analysis were carried out as above.

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