Synthesis of Carboxylic Acids through the Formation of C-C Bond between Saturated Hydrocarbons and CO in the Presence of $Mg/K_2S_2O_8$/TFA System

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Magnesium powder (Mg) promoted the carboxylation reaction of saturated hydrocarbons with carbon monoxide (CO) in the presence of potassium peroxodisulfate ($K_2S_2O_8$) in trifluoroacetic acid (TFA) to yield the corresponding carboxylic acids and alkyl trifluoroacetates. About 80% conversion of cyclohexane was achieved when 5 mmol of magnesium, 5 mmol of potassium peroxodisulfate, 3 mL of TFA, 1 mmol of cyclohexane, 50 atm of CO were used at 80 °C for 30 h.

The functionalization of saturated hydrocarbons has attracted increased attention for future organic syntheses because of enormous reserves of hydrocarbons at world's various areas. However, it is difficult and challenging to achieve such a goal due to the least reactivity of saturated hydrocarbons[1-4] and product selectivity of functionalized products.[5] Fujiwara et al.[6] and some others[7-9] have reported the transition metal catalyzed direct carboxylation of saturated hydrocarbons with CO to carboxylic acids using potassium peroxodisulfate ($K_2S_2O_8$), and oxygen as oxidants in trifluoroacetic acid (TFA) and also in water (H_2O). Recently, we reported that ytterbium oxide (Yb_2O_3) and ytterbium acetate ($Yb(OAc)_3$)[10] catalyze the carboxylation reaction of methane with CO in TFA and water, respectively.

One of the problems which has been encountered for all of those processes is the lower conversion of hydrocarbons. Therefore, it is necessary to overcome this problem to industrialize those processes. In this communication we would like to report the carboxylation reaction of saturated hydrocarbons with CO promoted by magnesium powder in TFA using $K_2S_2O_8$ as an oxidant as depicted in eq. 1.

$$\text{R-H} + \text{CO} \xrightarrow[\text{TFA}]{Mg/K_2S_2O_8} \underset{\mathbf{1}}{\text{R-COOH}} + \underset{\mathbf{2}}{\text{R-O-CO-CF}_3} \quad (1)$$

First, we have investigated the reaction of cyclohexane (5 mmol) with CO (20 atm) using various metals and salts in the presence of $K_2S_2O_8$ in TFA at 50 °C for 20 h. The results are summarized in Table 1. $K_2S_2O_8$ alone in this reaction yielded lower amount (0.8% yield based on cyclohexane) of **1** (entry 1). By addition of Mg powder (entry 2), the yield of **1** increased remarkably (2.4% yield based on cyclohexane). Magnesium oxide (MgO), zinc powder (Zn) and nickel powder (Ni) (entries 3, 7 and 9) gave the remarkable yields but less than entry 2. The other metals or metal compounds did not work significantly in this reaction of cyclohexane.

Then the effects of the amounts of Mg and $K_2S_2O_8$ on the yield of **1** under similar reaction conditions were investigated. The results are summarized in Figure 1. These experiments were carried out through two different ways, **a** and **b; a** with 5 mmol of $K_2S_2O_8$ and different amounts of Mg, and **b** with 5 mmol of Mg and different amounts of $K_2S_2O_8$. The yield of **1** in the reaction with 5 mmol of $K_2S_2O_8$ increases slowly with increasing the amount of Mg upto 2 mmol, giving **1** 0.14 mmol. After that the yield increases dramatically with increasing the amount of Mg till 5 mmol where the amount of **1** is 0.48 mmol. Further addition of Mg upto 8 mmol asymptotically increases the yield; however, a large excess of Mg caused a little decrease in the product (**a**). Almost similar phenomenon was observed in this reaction when various amounts of $K_2S_2O_8$ were added with a fixed (5 mmol) amount of Mg (**b**).

In order to make the reaction more efficient to yield **1**, the effect of temperature, amount of TFA and reaction time were

Table 1. Synthesis of cyclohexanecarboxylic acid from cyclohexane and CO[a]

Entry	Promoters	Yield[b]	
		mmol	%[c]
1	none	0.04	0.8
2	Mg	0.12	2.4
3	MgO	0.09	1.8
4	$MgCl_2$	0.03	0.6
5	$MgBr_2$	0.03	0.6
6	Mg[d]	0.01	0.2
7	Zn	0.07	1.4
8	$Zn(OAc)_2$	0.04	0.8
9	Ni	0.06	1.2
10	NiO	0.05	1.0
11	$Ni(OAc)_2$	0.03	0.6
12	Al	0.04	0.8
13	Ag(OAc)	0.02	0.4

[a] Reaction conditions: 25-mL autoclave, cyclohexane (5 mmol), metals or salts (1 mmol), $K_2S_2O_8$ (5 mmol), TFA (5 mL), 50 °C, 20 h. [b] Determined by GC. [c] Based on cyclohexane. [d] Reaction without $K_2S_2O_8$.

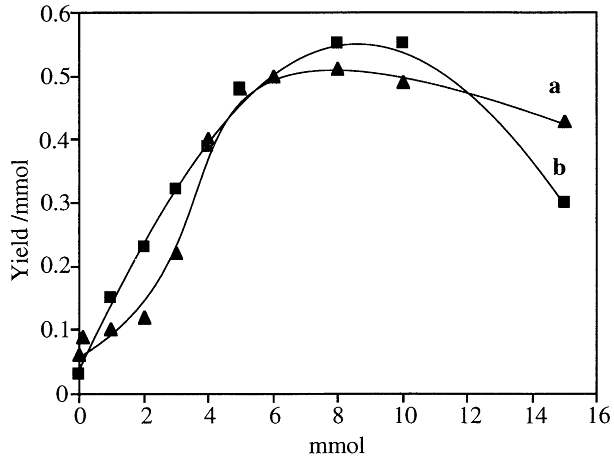

Figure 1. Effect of the amount of $K_2S_2O_8$ and Mg in the carboxylation reaction of cyclohexane (5 mmol) with CO (20 atm) in TFA (5 mL) at 50 °C for 20 h. (**a**) Effect of the amount of Mg using $K_2S_2O_8$ (5 mmol). (**b**) Effect of the amount of $K_2S_2O_8$ using Mg (5 mmol).

Table 2. Effect of temperature, amount of cyclohexane and reaction time[a]

Entry	Temperature (°C)	Cyclohexane (mmol)	Time (h)	Yield (%)[b]	
				1	**2**
1	60	5	20	17.8	1.6
2	80	5	20	35.0	6.2
3	90	5	20	29.4	4.4
4	80	1	20	64.0	2.8
5	80	5	30	36.8	7.4
6	80	5	40	37.8	8.2
7	80	1	25	66.0	1.0

[a] Reaction conditions: 25-mL autoclave, Mg (5 mmol), $K_2S_2O_8$ (5 mmol), CO (50 atm). [b] GC yields based on cyclohexane.

tested. The results are summarized in Table 2. It can be seen from this table that the yields of both **1** and **2** increase with increasing the temperature until 80 °C. Further increase of temperature results in decrease of the products (entry 3). About 36.8 and 37.8% yields of **1** were obtained when 5 mmol of cyclohexane was reacted for 30 and 40 h, respectively (entries 5 and 6) whereas 64 and 66% yields of **1** were obtained when 1 mmol of cyclohexane was used for 20 and 25 h, respectively (entries 4 and 7).

Then we investigated the carboxylation reaction of various saturated hydrocarbons using the optimum reaction conditions such as hydrocarbons (5 mmol) (methane 30 atm, 25 mmol), Mg (5 mmol), $K_2S_2O_8$ (5 mmol), TFA (3 mL), CO (50 atm), 80 °C, 30 h. The representative results obtained are listed in Table 3. As indicated in Table 3, the carboxylation reaction of methane resulted in low conversion (conversion 1.1% based on methane) with 96% selectivity of the product acetic acid (entry 1). The reaction of n-propane gave a moderate yield (11% conversion based on n-propane) of products iso- and n-propionic acids and iso-propyl trifluoroacetate (selectivity; 66 : 30 : 4) (entry 2). On the other hand, the cyclic saturated hydrocarbons listed in Table 3 gave higher yields. The reaction of cyclopentane gave 39% conversion with 66% selectivity of **1** (entry 3). The conversion of cyclohexane was about 43% when 5 mmol of cyclohexane was used (entry 4) whereas it was about 80% conversion with 83% selectivity of **1** when 1 mmol of cyclohexane was used (entry 5). The conversion of cycloheptane is 48% where the selectivity of the **1** is 31% (entry 6). The reason of low selectivity is unclear.

Several mechanistic aspects of the $Mg/K_2S_2O_8$ promoted carboxylation reaction of saturated hydrocarbons with CO yet remain unclear at present. The IR spectra of the solid phases of the reaction mixtures confirm the formation of magnesium trifluoroacetate $(CF_3COO)_2Mg$ and MgO in the reaction mixtures. In fact $(CF_3COO)_2Mg$ is formed in the reaction of Mg and TFA quantitatively.[11] The role of $K_2S_2O_8$ would be oxidation of $(CF_3COO)_2Mg$ to active oxygen containing magnesium oxide (Mg_2O_3) which would abstract a hydrogen atom (H) from hydrocarbon (R-H) to give alkyl radical (R•) that reacts with CO to give acyl radical (R-CO•).[12] R-CO• would be converted to carboxylic acid via the formation of mixed anhydride with TFA. Actually MgO in the various forms are active for the oxidative coupling of methane.[13,14] The lithium doped MgO (Li-MgO) and Ba-MgO[15] are very active catalysts for the oxidative coupling of lower hydrocarbons.

Table 3. $Mg/K_2S_2O_8$ promoted carboxylation reaction of various hydrocarbons[a]

Entry	Substrate	Product /mmol[b]		Conv./%[c]	Selectivity	
		1	**2**		**1**	**2**
1	CH_4	0.25	0.01	1[d]	96	4
2	$CH_3CH_2CH_3$	0.51[e]	0.02[f]	11[d]	96	4
3	$c\text{-}C_5H_{10}$	1.28	0.43	39	66	22
4	$c\text{-}C_6H_{12}$	1.75	0.31	43	82	14
5	$c\text{-}C_6H_{12}$	0.66	0.10	80[g]	83	13
6	$c\text{-}C_7H_{14}$	0.75	1.42	48	31	59

[a] Reaction conditions : 25-mL autoclave, methane (30 atm, 25 mmol), propane (7 atm, 5 mmol), other hydrocarbons (5 mmol), CO (50 atm), Mg (5 mmol), $K_2S_2O_8$ (5 mmol), TFA (3 mL), 80 °C, 30 h.
[b] Determined by GC. [c] Based on hydrocarbon. [d] NMR yield. [e] Isomer ratio is 31:69 (n:iso). [f] Isomer ratio is 0:100 (n:iso). [g] Cyclohexane (1 mmol).

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