

Synthesis of Carboxylic Acids through the Formation of C-C Bond between Saturated Hydrocarbons and CO in the Presence of Mg/K₂S₂O₈/TFA System

Mohammad Asadullah, Tsugio Kitamura, and Yuzo Fujiwara*

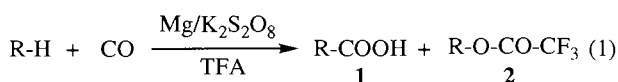
Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, Hakozaki, Fukuoka 812-8581

(Received March 1, 1999; CL-990133)

Magnesium powder (Mg) promoted the carboxylation reaction of saturated hydrocarbons with carbon monoxide (CO) in the presence of potassium peroxodisulfate (K₂S₂O₈) 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 hydrocarbons¹⁻⁴ and product selectivity of functionalized products.⁵ Fujiwara et al.⁶ and some others⁷⁻⁹ have reported the transition metal catalyzed direct carboxylation of saturated hydrocarbons with CO to carboxylic acids using potassium peroxodisulfate (K₂S₂O₈), and oxygen as oxidants in trifluoroacetic acid (TFA) and also in water (H₂O). Recently, we reported that ytterbium oxide (Yb₂O₃) 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 K₂S₂O₈ as an oxidant as depicted in eq. 1.



First, we have investigated the reaction of cyclohexane (5 mmol) with CO (20 atm) using various metals and salts in the presence of K₂S₂O₈ in TFA at 50 °C for 20 h. The results are summarized in Table 1. K₂S₂O₈ 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 K₂S₂O₈ 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 K₂S₂O₈ and different amounts of Mg, and **b** with 5 mmol of Mg and different amounts of K₂S₂O₈. The yield of **1** in the reaction with 5 mmol of K₂S₂O₈ increases slowly with

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

^aReaction conditions: 25-mL autoclave, cyclohexane (5 mmol), metals or salts (1 mmol), K₂S₂O₈ (5 mmol), TFA (5 mL), 50 °C, 20 h. ^bDetermined by GC. ^cBased on cyclohexane. ^dReaction without K₂S₂O₈.

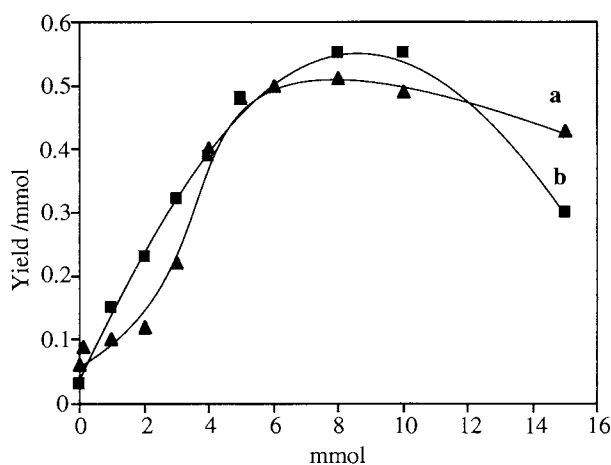


Figure 1. Effect of the amount of K₂S₂O₈ and Mg in the carboxylation reaction of cyclohexane (5 mmol) with CO (20 atm) in TFA (5 mL) at 50 °C for 20 h. (a) Effect of the amount of Mg using K₂S₂O₈ (5 mmol). (b) Effect of the amount of K₂S₂O₈ using Mg (5 mmol).

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 K₂S₂O₈ 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 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

^aReaction conditions: 25-mL autoclave, Mg (5 mmol), K₂S₂O₈ (5 mmol), CO (50 atm). ^bGC 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), K₂S₂O₈ (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/K₂S₂O₈ promoted

Table 3. Mg/K₂S₂O₈ 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 ₃ CH ₂ CH ₃	0.51 ^e	0.02 ^f	11 ^d	96	4
3	c-C ₅ H ₁₀	1.28	0.43	39	66	22
4	c-C ₆ H ₁₂	1.75	0.31	43	82	14
5	c-C ₆ H ₁₂	0.66	0.10	80 ^g	83	13
6	c-C ₇ H ₁₄	0.75	1.42	48	31	59

^aReaction conditions : 25-mL autoclave, methane (30 atm, 25 mmol), propane (7 atm, 5 mmol), other hydrocarbons (5 mmol), CO (50 atm), Mg (5 mmol), K₂S₂O₈ (5 mmol), TFA (3 mL), 80 °C, 30 h.

^bDetermined by GC. ^cBased on hydrocarbon. ^dNMR yield. ^eIsomer ratio is 31:69 (n:iso). ^fIsomer ratio is 0:100 (n:iso). ^gCyclohexane (1 mmol).

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 (CF₃COO)₂Mg and MgO in the reaction mixtures. In fact (CF₃COO)₂Mg is formed in the reaction of Mg and TFA quantitatively.¹¹ The role of K₂S₂O₈ would be oxidation of (CF₃COO)₂Mg to active oxygen containing magnesium oxide (Mg₂O₃) 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-MgO¹⁵ are very active catalysts for the oxidative coupling of lower hydrocarbons.

We are grateful for the Grants-in-Aid for Scientific Research on Priority Area No. 283 and Scientific Research (A) No. 09355031 from the Ministry of Education, Science, Sports, and Culture of Japan.

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