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$Mg/K_2S_2O_8$-promoted Direct Carboxylation of Saturated Hydrocarbons with CO

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Saturated hydrocarbons react with carbon monoxide in the presence of magnesium powder and potassium peroxodisulfate in trifluoroacetic acid (TFA) to afford the corresponding carboxylic acids as major products and alkyl trifluoroacetates as minor products in high yields. The use of equimolar amounts of magnesium (5 mmol) and $K_2S_2O_8$(5 mmol) is best for this reaction. Cyclohexane is carboxylated most effectively at 80 °C for 30 h using 50 atm CO, 3 ml of TFA and 1 mmol of cyclohexane, giving 80% conversion (95% conversion yield) based on cyclohexane. The reactivity of various saturated hydrocarbons has been determined by competitive reactions of equimolar amounts of cyclohexane (5 mmol) and another hydrocarbon (5 mmol). The order of decreasing reactivity obtained is cycloheptane > cyclohexane > cyclopentane > n-propane > methane. Copyright © 1999 John Wiley & Sons, Ltd.

Keywords: carboxylation; saturated hydrocarbon; cycloalkanecaboxylic acid; cycloalkyl trifluoroacetate; carbon monoxide; potassium peroxodisulfate

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INTRODUCTION

Hydrocarbons, the main component of petroleum oil and natural gas, are abundantly available and the cheapest chemicals in the world. Therefore, the direct conversion of hydrocarbons, especially saturated hydrocarbons, as a building block for functionalization products and higher hydrocarbons is one of the most promising routes for future organic syntheses because of enormous reserves of hydrocarbons in various areas of the world. Moreover, there has been a strong economic motivation to transform hydrocarbons directly and commercially into more valuable functionalized products such as alcohols, esters, aldehydes, ketones, acids, peroxides, amines and other solid or liquid products; over the last two decades it has greatly stimulated a large volume of commercial research to discover a fundamentally new route of hydrocarbon transformation, which constitutes an extremely important research field of contemporary chemistry. In addition, a new system of hydrocarbon transformation could help to reduce petroleum pollution and other important environmental problems. However, it is difficult and challenging to achieve such a goal due to the low reactivity of hydrocarbons and selectivity of functionalized products.[1–4]

The functionalized products (alcohols, aldehydes, acids etc.) are more reactive than the saturated hydrocarbons, and thus the thermodynamically more favorable complete combustion of hydrocarbons to carbon dioxide and water takes place. Therefore, the most sophisticated method should be developed under very mild reaction conditions that would convert hydrocarbons into more valuable liquid or solid chemicals and fuels in high yield without total oxidation. However, there is no such existing process satisfying these requirements. In recent years, scientists have been struggling to achieve such a goal through numerous research routes. These researches include the exploitation of both reactions that occur without the participation of metals or metal compounds, and reactions that involve metals or their compounds.

Both of these reactions usually occur in either the gas or the solution phase. Gas-phase functionalization reactions of hydrocarbons occur under severe conditions (high pressure and temperature) which makes them very unselective. These reactions are

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catalytic or non-catalytic.[5–12] The solution-phase hydrocarbon functionalizations seem to be a very promising field, due to their ease of operation under mild conditions, and hold the greatest promise of selectivity.[13] Cyclohexane oxidation in the liquid phase is one such process which has considerable industrial importance because it supplies raw materials such as cyclohexanol, cyclohexanone and adipic acid for the production of nylon-6 and nylon-66.

In the solution phase the reactions may be uncatalyzed,[14–17] or radical- or metal-catalyzed. The radical ion $SO_4^{\cdot -}$ which is generated from the thermal decomposition of $S_2O_8^{2-}$ at 100 °C in aqueous solution abstracts hydrogen from methane and ethane to generate alkyl radicals of the type $R^{\cdot}$, $R^{\cdot}$ radicals react further with $SO_4^{\cdot -}$ to form $ROSO_3^{-}$.[18] In the functionalization reactions of cyclohexane, various types of transition-metal compounds have been used, such as aluminophosphates of Co, Cr, Fe, Mn, Ti, and V;[19] manganese(II) salen complex;[20] copper salts and copper crown ether;[21] a cobalt(III) alkyl peroxide complex;[22] and titanium silicalite.[23] Various types of heteropolyacids[24–26] and methane mono-oxygenase of Fe(II)[27] are remarkably active to transform hydrocarbons to their oxidized products.

All the processes described above are oxidative transformations of hydrocarbons. Like oxidation, carboxylation of hydrocarbons to carboxylic acids is also an interesting and important functionalization process. No industrially suitable process for direct carboxylation of hydrocarbons to carboxylic acids is available at present. This process demands strong economic feasibility to produce carboxylic acids from hydrocarbons, due to the minimum energy and stage required. But until now only our group[28–39] and some others[40–46] have reported the direct catalytic conversion of hydrocarbons with CO to carboxylic acids using potassium peroxodisulfate ($K_2S_2O_8$), and oxygen as oxidants in the presence of transition-metal catalysts in trifluoroacetic acid (TFA) and also in water (H_2O). Recently, we reported that lanthanoid oxide (Yb_2O_3) promotes the direct conversion of methane to acetic acid[47] in TFA with $K_2S_2O_8$ as an oxidant. Ytterbium acetate also catalyzes the carboxylation reaction of methane with CO in water in the presence of sodium hypochlorite (NaClO) as an oxidant. Addition of a small amount of $Mn(OAc)_2$ increased the yield of acetic acid.[48] One of the problems which has been encountered for all of those processes is the lower conversion rate of hydrocarbons. Therefore, it is necessary to overcome this problem to make the direct carboxylation of hydrocarbons industrially feasible. In this paper, we report the carboxylation reaction of saturated hydrocarbons with CO promoted by magnesium powder (Mg) in TFA using $K_2S_2O_8$ as an oxidant.

EXPERIMENTAL

Materials

All reagents were of analytical grade and were used without further purification. Methane, propane and CO gases were purchased from Sumitomo Pure Chemical Co. Magnesium (Kanto Chemical Co., Inc.), TFA, $K_2S_2O_8$ (Wako Pure Chemical Industries, Ltd), cyclohexane (Kishida Chemical Co.), cycloheptane, cyclopentane (Nacalai Tesque, Inc.), adamantane (TCI Chemical Co.), nonanoic acid and n-butyric acid (Katayama Chemical Co.) were obtained commercially. Cyclopentyl trifluoroacetate, cyclohexyl trifluoroacetate, cycloheptyl trifluoroacetate and adamantyl trifluoroacetate have been prepared in our laboratory.

Apparatus

The reactions were carried out in a 25-ml stainless steel autoclave. The product mixtures were analyzed by a Shimadzu GC-8A gas chromatograph equipped with a flame ionization detector by using a 3 m × 3 mm i.d. stainless steel column packed with Unisole $10T + H_3PO_4$ ($5 + 0.5\%$) on 80/100 mesh Uniport HP with injection/detection temperatures of 220 °C and a column temperature of 160 °C for cycloalkanecarboxylic acids and 130 °C for acetic acid and butyric acid. The unreacted hydrocarbons and the product esters in the reaction mixtures were analyzed by the same gas chromatograph by using a 5 m × 3 mm i.d. stainless steel column packed with silicon OV-17 with injection/detection temperatures of 220 °C and a column temperature of 150 °C.

Procedure for the carboxylation of hydrocarbons

A 20-ml glass tube equipped with a Teflon-coated magnetic stirring bar (12 mm, octagonal) was charged with magnesium (5 mmol) and potassium peroxodisulfate (5 mmol). In the case of liquid hydrocarbons, the required amounts of hydrocarbon and TFA were added to the mixture successively.

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Then the tube was placed in a 25-ml stainless steel autoclave. The autoclave was closed and flushed with carbon monoxide three times to replace the air inside it, then pressurized with carbon monoxide. In the case of gaseous hydrocarbons, they were introduced after closing the autoclave. Then the autoclave was heated with stirring at 50 °C for 20 h. After the reaction, the autoclave was cooled on ice bath for 15 min and then opened. The contents of carboxylic acids in the liquid reaction mixtures were analyzed by GC-8A using nonanoic acid as an internal standard in the case of cycloalkanecarboxylic acids; in the case of acetic acid and butyric acid, n-butyric acid and acetic acid were used as internal standards, respectively. For determining the optimum reaction temperature, the reactions were carried out at different temperatures from room temperature to 90 °C. The experiments on the time course of the reaction were performed from 0.5 h to 90 h. To determine the optimum amounts of cyclohexane and TFA and the pressure of CO, the reactions were carried out by varying the amount of each of these. The other conditions were fixed in those cases.

Procedure for the competitive reaction

A 20-ml glass tube equipped with a Teflon-coated magnetic stirring bar (12 mm, octagonal) was charged with magnesium (5 mmol), potassium peroxodisulfate (5 mmol), and then TFA (3 ml). Then equimolar amounts of cyclohexane (5 mmol) and any other liquid hydrocarbon (5 mmol) were added in the mixture. The tube was placed in a 25-ml stainless steel autoclave. The autoclave was closed and flushed with CO three times to replace the air inside it, then pressurized with CO (50 atm). In the case of gaseous hydrocarbons, 7 atm (5 mmol) of gas was introduced after pressurizing with CO (50 atm). Then the autoclave was heated with stirring at 80 °C for 5 h. After the reaction was completed, the autoclave was cooled on an ice bath for 15 min and then opened. The product contents were analyzed in the same way as described above.

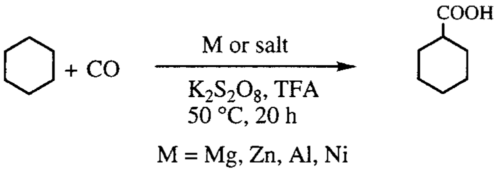
Table 1 Effect of metal powders and salts on the carboxylation of cyclohexane[a]

Entry	Metal or salt	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 $K_2S_2O_8$.

RESULTS AND DISCUSSION

We have investigated the carboxylation of cyclohexane with CO in the presence of metal powders or metal salts and $K_2S_2O_8$ in TFA (Eqn [1]). The reaction was carried out in a 25-ml autoclave using a glass insert charged with metal powders or salts, $K_2S_2O_8$, TFA and cyclohexane at 50 °C for 20 h. The representative results obtained are summarized in Table 1.



[1]

The reaction of cyclohexane with CO in the presence of $K_2S_2O_8$ alone yielded a lower amount (0.04 mmol, 0.8% yield based on cyclohexane) of cyclohexanecarboxylic acid (entry 1). By addition of magnesium powder (entry 2), the yield of cyclohexanecarboxylic acid was increased remarkably (2.4% yield based on cyclohexane). Although zinc powder and nickel powder (entries 7 and 9) gave slightly higher yields than that of entry 1, they were much less than entry 2. Aluminum powder (entry 12) did not work significantly in this carboxylation of cyclohexane. All the metal oxides and salts used in this reaction (entries 3, 4, 5, 8, 10, 11 and 13) gave lower yields than the blank experiment (entry 1). On the other hand, the reaction with magnesium alone in TFA gave a very low yield (entry 6).

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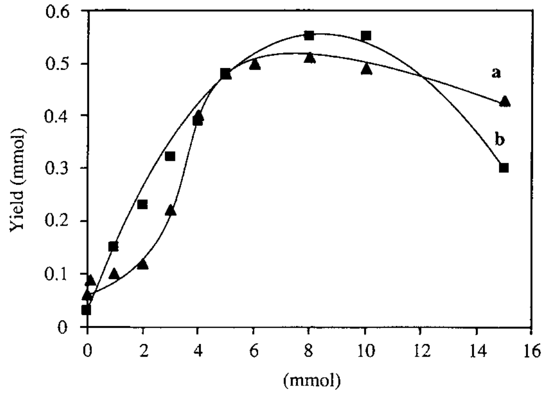

Figure 1 Effect of the amounts of $K_2S_2O_8$ and Mg on the carboxylation of cyclohexane (5 mmol) with CO (20 atm) in TFA (5 ml) at 50 °C for 20 h: (**a**) effect of the amount of Mg using $K_2S_2O_8$ (5 mmol); (**b**) effect of the amount of $K_2S_2O_8$ using Mg (5 mmol).

Since it become apparent that magnesium powder with $K_2S_2O_8$ promotes the carboxylation of cyclohexane significantly, we investigated various factors that affected the efficiency of the reaction of Eqn [1].

First, we carried out experiments to determine the optimum amounts of magnesium and $K_2S_2O_8$ for the reaction. The results are depicted in Fig. 1. These experiments were carried out in two different ways, **a** and **b: a** with 5 mmol of $K_2S_2O_8$ and different amounts of magnesium, and **b** with 5 mmol of magnesium and different amounts of $K_2S_2O_8$. The yield of cyclohexanecarboxylic acid in the reaction with 5 mmol of $K_2S_2O_8$ increases slowly as the amount of magnesium is increased to 2 mmol, giving 0.14 mmol of the cyclohexanecarboxylic acid. After that the yield increases dramatically as the amount of magnesium is increased, up to 5 mmol where the yield of product is 0.48 mmol. Further addition of magnesium up to 8 mmol increases the yield asymptotically, but a large excess of magnesium causes a slight decrease in the product (**a**). An 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 magnesium (**b**).

Comparing the experiments **a** and **b, a** proceeded through a short induction period. It is also noted that the yield was decreased sharply by addition of a large amount of $K_2S_2O_8$ compared with the case of the magnesium. One explanation of this trend is that the addition of a large excess of $K_2S_2O_8$ in the reaction mixture with a fixed amount of magnesium makes the Mg/$K_2S_2O_8$ ratio lower than unity, which again results in an induction mood. From these results we decided that 5 mmol each of magnesium and $K_2S_2O_8$ are best for this reaction. Thus the following experiments were all carried out using these amounts.

All the chemical reactions are very sensitive to the temperature, with respect to conversion yield and selectivity of the desired product. Therefore, we investigated the optimum reaction temperature. The experiments were performed from room temperature to 90 °C. Representative results are shown in Fig. 2. Curves **1** and **2** are the variation of the yields of cyclohexanecarboxylic acid (the major product) and cyclohexyl trifluoroacetate (a minor product) with temperature, respectively. The reaction proceeds even at room temperature, giving both major and minor products in 0.25 mmol and 0.04 mmol yields, respectively. The yields increases sharply with increasing the temperature up to 80 °C, where the maximum yield of cyclohexanecarboxylic acid is 1.75 mmol (35% yield based on cyclohexane) and of cyclohexyl trifluoroacetate it is 0.31 mmol (6.2% yield based on cyclohexane). After that the yields decrease with increasing the temperature. Several reasons for the decreasing trend of products may be considered here. One may be the self-decomposition of cyclohexanecarboxylic acid and cyclohexyl trifluoroacetate at high temperatures to smaller molecules, which are obtained on the GC chart as several peaks. The

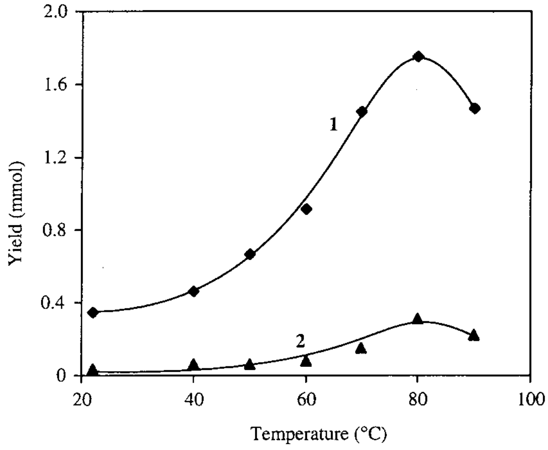

Figure 2 Effect of temperature on the carboxylation of cyclohexane (5 mmol) in the presence of Mg (5 mmol), $K_2S_2O_8$ (5 mmol) and CO (50 atm) in TFA (3 ml) for 20 h: (**1**) yield of cyclohexanecarboxylic acid; (**2**) yield of cyclohexyl trifluoroacetate.

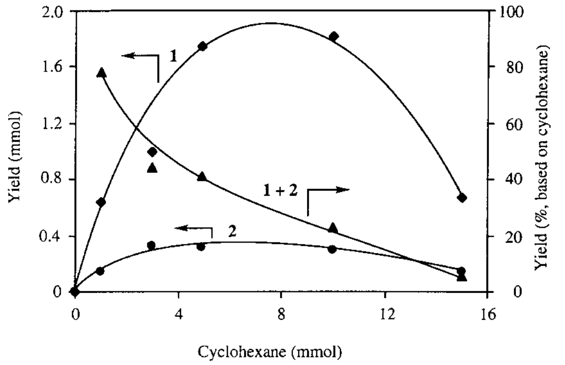

Figure 3 Effect of the amount of cyclohexane on the carboxylation reaction in the presence of Mg (5 mmol) and $K_2S_2O_8$ (5 mmol) in TFA (3 ml) using 50 atm of CO pressure for 20 h: (**1**) yield of cyclohexanecarboxylic acid; (**2**) yield of cyclohexyl trifluoroacetate; (**1** + **2**) yield of total products based on cyclohexane.

other possibility is the thermal decomposition of $K_2S_2O_8$ which would cause insufficiency of oxidant in the reaction mixture. Moreover, the solubility of the gaseous educt CO usually decreases at high temperature, so the carboxylation step in the reaction cycle inevitably becomes slow due to the low concentration of CO in the liquid phase at high temperature. Considering the results of Fig. 2, any further experiments were carried out at the optimum temperature, 80 °C.

Then we investigated the effect of the amount of cyclohexane in the magnesium-promoted carboxylation reaction in the presence of $K_2S_2O_8$ in TFA (Fig. 3). Careful examination of Fig. 3 reveals that the yield of cyclohexanecarboxylic acid increases constantly as the amount of cyclohexane is increased to 5 mmol, where the yield of cyclohexanecarboxylic acid is 1.75 mmol. Then the yield becomes almost constant until the addition of 10 mmol of cyclohexane, whereas the further addition of cyclohexane causes a sharp decrease in cyclohexanecarboxylic acid (curve **1**). The product cyclohexyl trifluoroacetate increases to attain a maximum value of 0.32 mmol at addition of 5 mmol of cyclohexane. Further addition of cyclohexane does not change the yield of cyclohexyl trifluoroacetate (curve **2**). On the other hand, the yield based on cyclohexane of the total product is the highest (78%) when the smallest amount (1 mmol) of cyclohexane was used. Then the total yield decreases gradually with increasing amount of cyclohexane added. The amount of unreacted cyclohexane increases with increasing addition of cyclohexane in the reaction mixture. Therefore, although the amount of the product (in mmol) increases until the addition of the optimum amount of cyclohexane, the percentage yield based on cyclohexane decreases [curve (**1** + **2**)].

Finally, we investigated the effect of time-course on the carboxylation reaction of cyclohexane. The experiments were carried out from 0.5 to 90 h. From Fig. 4 it can be seen that the yield of cyclohexanecarboxylic acid increases dramatically until 20 h. After that the yield increases asymptotically until 40 h. Over a prolonged time the yield of cyclohexanecarboxylic acid decreases slowly (curve **1**). On the other hand, the yield of cyclohexyl trifluoroacetate increases with the time gradually until 60 h and finally it, also, decreases slowly (curve **2**).

Then we investigated the carboxylation of various saturated hydrocarbons using the optimum reaction conditions: hydrocarbon (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. Representative results obtained are listed in Table 2. As indicated in Table 2, the carboxylation of methane resulted in low conversion (1.1% based on methane) with 96% selectivity of the product acetic acid (entry 1). The reaction of n-propane [using 7 atm (5 mmol)] gave a moderate yield (10.6% conversion based on n-propane) of products isopropionic acid, n-propionic acid and isopropyl trifluoroacetate (selectivity 66:30:4) (entry 2). On the other hand, the cyclic saturated hydrocarbons listed in Table 2 gave higher yields.

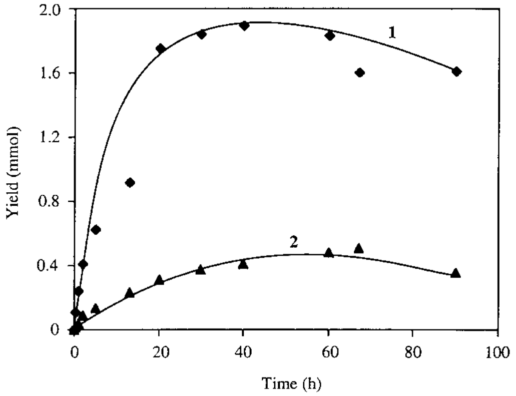

Figure 4 Effect of time-course on the carboxylation reaction of cyclohexane (5 mmol) with CO (50 atm) in the presence of Mg (5 mmol) and $K_2S_2O_8$ (5 mmol) at 80 °C: (**1**) yield of cyclohexanecarboxylic acid; (**2**) yield of cyclohexyl trifluoroacetate.

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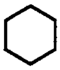
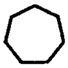
Table 2 Mg/$K_2S_2O_8$-promoted carboxylation of various hydrocarbons[a]

$$\mathrm{R{-}H + CO \xrightarrow[\text{TFA, 80 °C, 30 h}]{\mathrm{Mg/K_2S_2O_8}} \underset{\mathbf{1}}{R{-}COOH} + \underset{\mathbf{2}}{R{-}O{-}CO{-}CF_3}} \qquad [2]$$

		Product (mmol)[b]		Conversion		Conversion yield (%)[d]
Entry	Hydrocarbon	**1**	**2**	(mmol)	(%)[c]	
1	CH_4	0.25	0.01	0.26[e]	1.1	100.0 (96:4)
2		*n*-0.16 *iso*-0.35	0.02	0.53[e]	10.6	100.0 (30:66:4)
3		1.28	0.43	1.95	39.0	87.7 (66:22)
4		1.75	0.31	2.15	43.0	95.8 (82:14)
5		0.66	0.10	0.80[f]	80.0	95.0 (83:13)
6		0.75	1.42	2.40	48.0	90.4 (31:59)
7		0.72	0.12	0.90	18.0	93.3 (80:13)

[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] Numbers in parentheses are the ratio of **1**:**2**.
[e] NMR yield.
[f] Cyclohexane (1 mmol).

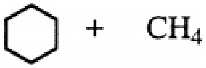
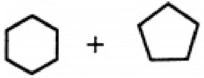
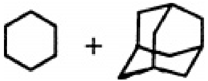
The reaction of cyclopentane gave 39% conversion with 66% selectivity of cyclopentanecarboxylic acid (entry 3). The conversion of cyclohexane in this reaction was about 43% when 5 mmol of cyclohexane was used (entry 4), whereas there was about 80% conversion with 83% selectivity of cyclohexanecarboxylic acid when 1 mmol of cyclohexane was used (entry 5).

It is interesting that the major product of the carboxylation of cycloheptane was esterified, and the carboxylated product was a minor product. The total conversion of cycloheptane is 48% and the selectivity of the cycloheptyl trifluoroacetate is 59% (entry 6). Adamantane gave a lower yield in this reaction, 18% conversion.

Finally, we performed competitive reactions of hydrocarbons to determine the reactivity using equimolar amounts of cyclohexane (5 mmol) and another hydrocarbon (5 mmol). The results are summarized in Table 3, from which one can see that the conversion rate of cycloheptane is the highest of all the hydrocarbons listed in Table 3 and that of methane is the lowest. The reactivity order of the conversion is: cycloheptane $>$ cyclohexane $>$ cyclopentane $>$ n-propane $>$ methane. Although the conversion rate of cyclohexane is a little lower than that of cycloheptane ($\mathbf{b}/\mathbf{a} = 1.11$), the carboxylation rate ($\mathbf{b}_1/\mathbf{a}_1 = 0.41$) is much higher than that of cycloheptane and also other hydrocarbons. The carboxylation reactivity was found to be in the following order: cyclohexane $>$ cyclopentane $>$ cycloheptane $>$ n-propane $>$ methane. On the other hand, the esterification reactivities of cycloheptane ($\mathbf{b}_2/\mathbf{a}_2 = 7.5$) and cyclopentane ($\mathbf{b}_2/\mathbf{a}_2 = 1.4$) are

Table 3 Competitive reaction of cyclohexane with various hydrocarbons[a]

$$\underset{\mathbf{a}}{\mathrm{Cy-H}} + \underset{\mathbf{b}}{\mathrm{R-H}} + \mathrm{CO} \xrightarrow[\mathrm{TFA,\ 80\,^{\circ}C,\ 5\,h}]{\mathrm{Mg/K_2S_2O_8}} \underset{\mathbf{a_1}}{\mathrm{Cy-COOH}} + \underset{\mathbf{b_1}}{\mathrm{R-COOH}} + \underset{\mathbf{a_2}}{\mathrm{Cy-O-CO-CF_3}} + \underset{\mathbf{b_2}}{\mathrm{R-O-CO-CF_3}} \quad [2]$$

Entry	Substrates	Conv. (%)		Conv. yield (%)[b]				Reactivity ratio		
		a	**b**	**a_1**	**a_2**	**b_1**	**b_2**	**b/a**	**b_1/a_1**	**b_2/a_2**
1		14.4	1.4	83	11	100	0	0.10	0.12	—
2		12.4	1.8	77	13	100	0	0.15	0.19	—
3		11.0	6.2	85	9	68	23	0.56	0.45	1.40
4		9.0	10.0	87	9	32	60	1.11	0.41	7.50
5		13.4	3.8	78	13	84	5	0.28	0.31	0.11

[a] Reaction conditions: 25-ml autoclave, cyclohexane (5 mmol), methane (7 atm, 5 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, 5 h.

[b] GC yields based on converted hydrocarbons.

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higher than that of cyclohexane. The esterification reactivity order was found to be: cycloheptane $>$ cyclopentane $>$ cyclohexane $\gg$ propane, methane. The esterification products of methane and n-propane from this competitive reaction were not detected by NMR spectroscopy. In the case of adamantane, it sublimed from the solution phase under the reaction conditions: therefore, the result of this experiment would not be accurate (entry 5).

Several mechanistic aspects of the $Mg/K_2S_2O_8$-promoted carboxylation reaction of saturated hydrocarbons with CO remain unclear at present. Recently Lin and Sen[45] reported the $K_2S_2O_8$-mediated carboxylation of methane and ethane with CO in water to give acetic acid and/or propionic acid. In this reaction, sulfate radical anion ($SO_4^{\cdot -}$) generated from $S_2O_8^{2-}$ abstracts a hydrogen atom from methane and ethane to form the corresponding alkyl radicals, which are trapped by CO, and the resultant acyl radicals are converted into the carboxylic acids. But in our reaction magnesium and $K_2S_2O_8$ together in TFA gave remarkable yields of carboxylic acids whereas magnesium alone gave low yields of carboxylic acids, and $K_2S_2O_8$ alone promoted the carboxylation of saturated hydrocarbons but slightly. The much higher yields of the carboxylic acids from the carboxylation of saturated hydrocarbons promoted by the combination of magnesium and $K_2S_2O_8$, compared with the yields of the reaction promoted by $K_2S_2O_8$ alone, indicate that the mechanisms of the reactions are different.

Moreover, this carboxylation reaction of saturated hydrocarbons proceeded remarkably well with the addition of magnesium oxide (MgO). We also performed a stepwise reaction in which the mixture of magnesium and $K_2S_2O_8$ was stirred in TFA for 20 h at 80 °C under 5 atm of nitrogen. Then 5 mmol of cyclohexane and 50 atm of CO were added to the reaction mixture and stirred at the same temperature for an additional 20 h. This reaction also gave the same amount of products (entry 4, Table 2). The IR spectra of the solid phases of the stepwise reactions confirm the formation of magnesium trifluoroacetate [$(CF_3COO)_2Mg$] and MgO in the reaction mixtures. $(CF_3COO)_2Mg$ is formed quantitatively in the reaction of magnesium and TFA.[49] In the presence of other reactants, $K_2S_2O_8$ and CO, $(CF_3COO)_2Mg$ may be converted into MgO. The evidence described above supports the idea that the MgO is an active species in this reaction. MgO would abstract a hydrogen atom (H) from the hydrocarbon (R—H) to give an alkyl radical (R·), which reacts with CO to give an acyl radical (R—CO·). R—CO· would be oxidized by another MgO to give an acyl cation ($R—CO^+$), which reacts with TFA to form a mixed anhydride ($R—CO—O—OC—CF_3$). Then the anhydride reacts with another TFA molecule to give the product carboxylic acid (R—COOH) and $(CF_3CO)_2O$. MgO in various forms is active in the oxidative coupling of methane.[50–52] Lithium-doped MgO (Li–MgO)[53–58] and Ba–MgO[59] are very active catalysts for the oxidative coupling of lower hydrocarbons.

CONCLUSION

We have found that magnesium metal significantly promotes the carboxylation of saturated hydrocarbons with CO in the presence of $K_2S_2O_8$ in TFA. Cyclohexane is carboxylated most effectively by equimolar amounts of magnesium (5 mmol) and $K_2S_2O_8$ (5 mmol), at 80 °C for 30 h using cyclohexane (5 mmol), TFA (3 ml) and CO (50 atm), giving cyclohexanecarboxylic acid as a major product in 83% conversion yield and cyclohexyl trifluoroacetate as a minor product in 13% conversion yield. From the competitive reactions, we found that the conversion reactivity increases with increasing number of carbon atoms, in the following order: methane $<$ propane $<$ cyclopentane $<$ cyclohexane $<$ cycloheptane. On the other hand, the orders of carboxylation reactivity and esterification reactivity are different from that of the conversion reactivity. The order of carboxylation reactivity is: methane $<$ propane $<$ cycloheptane $<$ cyclopentane $<$ cyclohexane. The order of esterification reactivity is: methane, n-propane $\ll$ cyclohexane $<$ cyclopentane $<$ cycloheptane.

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