

CaCl₂-Catalyzed Functionalization of Saturated Hydrocarbons with CO to Carboxylic Acids and Esters

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The functionalization of saturated hydrocarbons such as ethane, propane, cyclopentane, cyclohexane, cycloheptane, and cyclooctane with CO by CaCl₂ catalyst in the presence of K₂S₂O₈ and CF₃COOH was studied. In this reaction carboxylic acids were formed as dominant products and alkyl trifluoroacetates were formed as by-products. In the reaction of propane, isobutyric acid was the main product and *n*-butyric acid and isopropyl trifluoroacetate were the by-products in 95% total yield based on propane when 1 bar of propane reacted with 30 bar of CO in the presence of CaCl₂ (0.5 mmol), K₂S₂O₈ (5 mmol), and CF₃COOH (5 ml) at 80°C for 24 h. Ethane gave about 88% total yield; however, in that case 23% acetic acid was formed by the oxidation of ethane. Cyclopentane, cyclohexane, and cycloheptane underwent reaction, giving about 44, 33, and 12% total yields, respectively. However, cyclooctane did not undergo this reaction. The activation parameters for the reaction of propane (5 bar) with CO (30 bar) have been determined to be $E_a = 130.3, 138.0, \text{ and } 153.8 \text{ kJ/mol}$; $A = 7.14 \times 10^{13}, 5.83 \times 10^{14}, \text{ and } 5.80 \times 10^{16} \text{ s}^{-1}$; $\Delta H^\ddagger = 128.0, 134.7, \text{ and } 150.5 \text{ kJ/mol}$; $\Delta S^\ddagger = 10.3, 28.6, \text{ and } 66.8 \text{ J/mol K}$; and $\Delta G_{353}^\ddagger = 124.4, 123.9, \text{ and } 126.9 \text{ kJ/mol}$ for the products isobutyric acid, *n*-butyric acid, and isopropyl trifluoroacetate, respectively. © 2000 Academic Press

Key Words: saturated hydrocarbons; carbon monoxide; calcium dichloride; carboxylic acid; catalysis.

INTRODUCTION

The lower alkanes such as ethane and propane are abundantly available in the world, being utilized as clean burning fuels for energy supply. For example, about 200 million tons of liquid petroleum gas (LPG) are supplied in a year, most of which is being consumed as fuel. Thus, a new chemical process for direct and selective functionalization of lower alkanes to upgraded products such as alcohols, aldehydes, ketones, acids, etc. under mild conditions is one of the most promising methods for future organic synthesis (1, 2). However, the process remains challenging because of the low reactivity of lower hydrocarbons and poor selectivity of their products. Scientists

have conducted much theoretical and practical research on propane transformations to useful products such as oxidative dehydrogenation of propane to propene (3–7), oxidation of propane to alcohol (8, 9) and acrylic acid (10–12), carbonylation of propane with CO to butanal (13), amoxidation of propane to acrylonitrile (14, 15), vapor-phase epoxidation of propane (16), and aminomethylation of propane with *N,N*-dialkylmethylamine *N*-oxides to *N,N*-dialkylaminomethylated propane (17).

Carboxylation of propane with CO to isobutyric and *n*-butyric acids is another important functionalization process; however, much fewer examples of this reaction are reported (18). Recently, we found that Mg powder (19, 20) and Co(OAc)₂ (21) promote and catalyze the carboxylation of propane, respectively. The former is not catalytic and gives a low yield but the latter gives moderate yield; however, the catalyst lifetime is short. Moreover, Co(OAc)₂ catalyst is very selective to carboxylate only propane. In this paper, we describe the high-yield functionalization of propane to isobutyric acid (1), *n*-butyric acid (2), and isopropyl trifluoroacetate (3) by highly efficient and cheap CaCl₂ catalyst in the presence of K₂S₂O₈ and CF₃COOH (TFA). The reactions of ethane and cyclopentane also give high yields of their corresponding carboxylic acids and esters.

METHODS

Carboxylation Reaction of Propane

The catalyst and K₂S₂O₈ were placed in a 25-ml stainless steel autoclave equipped with a Teflon-coated magnetic stirring bar (12 mm, octagonal). Next, 5 ml of TFA was introduced into the autoclave which was then closed and flushed with propane three times to replace the air inside and finally pressurized with the desired pressures of propane and CO. The autoclave was then heated with stirring at a fixed temperature in an oil bath for the desired length of time. After the reaction was finished, the autoclave was cooled in an ice bath for 15 min and then opened. About 80 mg of an internal standard (*n*-valeric acid) was

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added to the reaction mixture and stirred for 5 min. The carboxylic acids were analyzed by gas chromatography using a Shimadzu GC-8A equipped with a flame ionization detector with a 3-m \times 3.0-mm-i.d. stainless steel column packed with Unisole10T + H₃PO₄ (5 + 0.5)% on 80/100 mesh Uniport HP at an injection/detection temperature of 220°C and a column temperature of 130°C. The ester product of propane was characterized by NMR spectroscopy.

For the determination of the optimum temperature, amount of catalyst, pressure of carbon monoxide, amount of K₂S₂O₈, pressure of propane, amount of TFA, and time course, we varied the scale in each of the experiments.

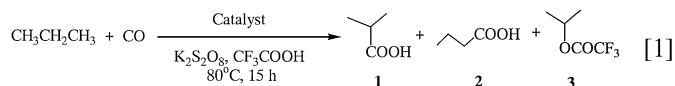
The experiments on the carboxylation of ethane, cyclopentane, cyclohexane, cycloheptane, and cyclooctane were carried out in the same way. However, the ester products of these hydrocarbons were analyzed by using the same gas chromatograph with a 3-m \times 3-mm-i.d. stainless steel column packed with Silicone OV-17 under the conditions of an injection/detection temperature of 220°C and a column temperature of 100°C.

After the solution phase is separated from the reaction mixture, the solvent may be separated from the products by distillation because the boiling point difference is sufficient for distillation. The solid spent catalyst and reagents were gathered and treated with water to give a clear solution which is now under investigation.

RESULTS AND DISCUSSION

Effect of Alkaline Earth Compounds on the Carboxylation Reaction of Propane

First, we investigated the catalytic performance of alkaline earth compounds for the carboxylation reaction of propane with CO in the presence of K₂S₂O₈ and TFA at 80°C for 15 h in a 25-ml stainless steel autoclave. The reaction gives isobutyric acid (**1**) as a dominant product and *n*-butyric acid (**2**) and isopropyl trifluoroacetate (**3**) as by-products as shown in reaction [1]. The results of these experiments are demonstrated in Table 1.



This reaction proceeded in very low yields of **1**, **2**, and **3** (0.02, 0.01, and 0.12 mmol, respectively) when K₂S₂O₈ was used alone. The combination of Ca compounds with K₂S₂O₈ under the same reaction conditions gave remarkably high yields of all the products.

Of the Ca compounds tested, CaCl₂ gives the most remarkable yields of **1**, **2**, and **3** (0.62, 0.31, and 0.20 mmol, respectively; about 25% yield based on propane) where the turnover number is 2.26 based on Ca atoms. CaSO₄ did not bring about this reaction of propane significantly. The

TABLE 1
Effect of Alkaline Earth Compounds on the Carboxylation Reaction of Propane with CO^a

Catalyst	Yield				TON ^d
	mmol ^b			% ^c	
	1	2	3		
None	0.02	0.01	0.12	3.3	—
CaCl ₂ · 2H ₂ O	0.62	0.31	0.20	25.0	2.26
CaO	0.54	0.19	0.19	20.3	1.84
CaCO ₃	0.46	0.16	0.12	16.3	1.48
Ca(OAc) ₂ · 2H ₂ O	0.31	0.11	0.10	11.5	1.04
Ca(acac) ₂ · 2H ₂ O	0.10	0.04	0.05	4.2	0.38
Ca(OH) ₂	0.01	0.01	0.04	1.3	0.12
CaSO ₄ · 2H ₂ O	Trace	—	0.15	3.3	0.30
Mg ^e	0.35	0.16	0.02	10.6	0.11
MgCl ₂	Trace	—	Trace	—	—
BaCl ₂	Trace	Trace	Trace	—	—

^a Conditions: 25-ml autoclave, propane (6 bar, 4.54 mmol), CO (30 bar), alkaline earth compound (0.5 mmol), K₂S₂O₈ (4 mmol), and TFA (5 ml) at 80°C for 15 h.

^b Determined by GC.

^c Based on propane.

^d Based on Ca.

^e Conditions: Mg (5 mmol), TFA (3 ml), 30 h.

other metal compounds, MgCl₂ and BaCl₂, are also inactive in this reaction. Although Mg powder gives a remarkable result (19, 20), it is not catalytic. Therefore, it is obvious that CaCl₂ is a significant catalyst in the carboxylation reaction of propane.

Effect of Temperature

Since CaCl₂ is a catalyst for the carboxylation of propane, the reaction was optimized. First the optimum temperature for this reaction was determined. The results are shown in Fig. 1.

This reaction proceeds at low temperature even at room temperature to give low yields of **1** and **2** (0.08 and 0.04 mmol, respectively) and trace amounts of **3**. The yields of **1** and **2** increase with increasing temperature until 75–80°C and then the yields gradually decrease with further increases of temperature. The decreasing trend may be due to the thermal or catalytic decomposition of acid products at high temperature to smaller molecular products which are actually observed on the GC chart as several peaks. Moreover, the solubility of CO severely decreases with increasing temperature. Thus, the carboxylation reaction becomes slower due to the low concentration of CO in the solution.

On the other hand, the product **3** gradually increases with increasing temperature beyond 75°C, maybe through a different mechanism. Thus, it is apparent that 75–80°C is the best temperature for the formation of acid products which are the main target of this work. Therefore, the following

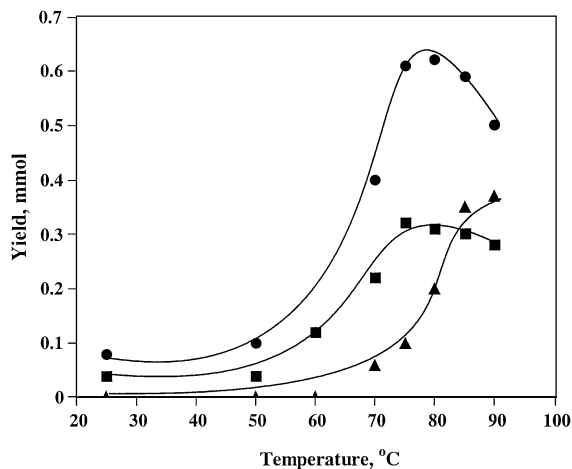


FIG. 1. Effect of temperature on the yields of CaCl_2 (0.5 mmol)-catalyzed carboxylation reaction of propane (6 bar, 4.54 mmol) with CO (30 bar) in the presence of $\text{K}_2\text{S}_2\text{O}_8$ (4 mmol) in TFA (5 ml) for 15 h. Yield of isobutyric acid (**1**) (●), *n*-butyric acid (**2**) (■), and isopropyl trifluoroacetate (**3**) (▲).

reactions were carried out at an optimum temperature of 80°C.

Effect of the Amount of $\text{K}_2\text{S}_2\text{O}_8$

We then investigated the optimum amount of $\text{K}_2\text{S}_2\text{O}_8$ for this reaction. The amount of $\text{K}_2\text{S}_2\text{O}_8$ was varied from 1 to 12 mmol while the other conditions were kept constant. The results of this experiments are shown in Fig. 2. This figure reveals that the reaction of propane with CO to corresponding acids did not take place in the absence of $\text{K}_2\text{S}_2\text{O}_8$. Very small amounts of **1**, **2**, and **3** were formed

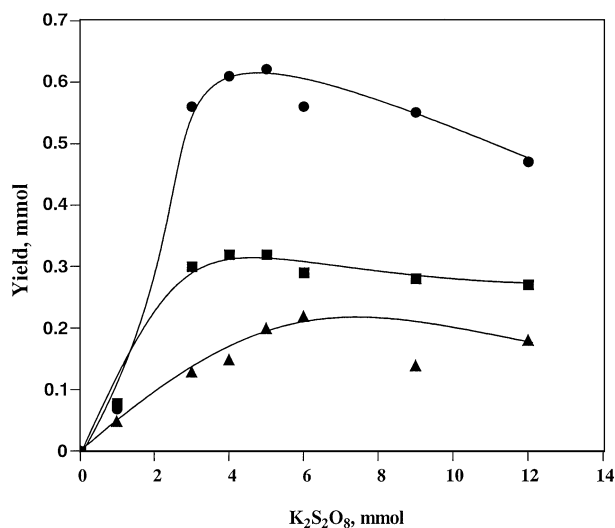


FIG. 2. Effect of the amount of $\text{K}_2\text{S}_2\text{O}_8$ on the yields of CaCl_2 (0.5 mmol)-catalyzed carboxylation reaction of propane (6 bar, 4.54 mmol) with CO (30 bar) in TFA (5 ml) at 80°C for 15 h. Yield of isobutyric acid (**1**) (●), *n*-butyric acid (**2**) (■), and isopropyl trifluoroacetate (**3**) (▲).

when 1 mmol of $\text{K}_2\text{S}_2\text{O}_8$ was used in the reaction mixture. With increasing amounts of $\text{K}_2\text{S}_2\text{O}_8$, the yields of **1** and **2** increased up to 3 mmol of $\text{K}_2\text{S}_2\text{O}_8$. Addition of $\text{K}_2\text{S}_2\text{O}_8$ above 3 mmol causes an asymptotic increment of the yields to give the maximum values (0.62 and 0.32 mmol of **1** and **2**, respectively) up to 5 mmol of $\text{K}_2\text{S}_2\text{O}_8$. Further increasing the amount of $\text{K}_2\text{S}_2\text{O}_8$ causes a slight decrease in the yields of **1** and **2** while the yield of product **3** increases with increasing amount of $\text{K}_2\text{S}_2\text{O}_8$ up to 6 mmol. Excess of $\text{K}_2\text{S}_2\text{O}_8$ beyond 6 mmol did not alter the yields of **3**. In the presence of a large excess of $\text{K}_2\text{S}_2\text{O}_8$, the overoxidation of the products **1** and **2** may occur which would lead to a decrease of the yields.

Moreover, increasing the amount of $\text{K}_2\text{S}_2\text{O}_8$ resulted in an increment of the density of the slurry inside the autoclave which decreased the rate of rotation of the magnetic stirring bar. The yield of this reaction apparently depends on the stirring rate which is also experimentally proved. Thus, the yield gradually decreases with increasing amount of $\text{K}_2\text{S}_2\text{O}_8$.

Effect of CO Pressure

The concentration of CO in the liquid phase is very important for the formation of the C–C bond in the carboxylation reaction of propane with CO. Moreover, in this reaction, CO acts not only as a carbonyl source but also as a reducing agent. Both of these properties of CO increase with increasing pressure. Therefore, the effect of various pressures of CO in this reaction was investigated. The yields are shown as a function of pressure in Fig. 3. This reaction proceeded in low yields of **1** and **2** but high yield of **3** under low pressure or absence of CO; under 1 bar of CO pressure, the yields are 0.09, 0.13, and 0.63 mmol of **1**, **2**, and **3**, respectively. On the other hand, the reaction gives 0.65 mmol of **3** only in the absence of CO.

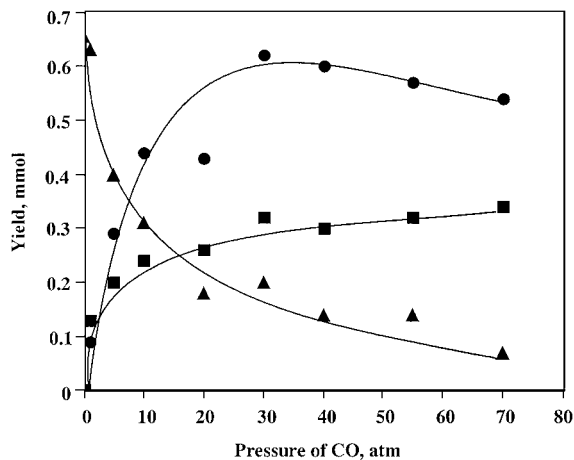


FIG. 3. Effect of CO pressure on the yields of CaCl_2 (0.5 mmol)-catalyzed carboxylation reaction of propane (6 bar, 4.54 mmol) in the presence of $\text{K}_2\text{S}_2\text{O}_8$ (5 mmol) and CF_3COOH (5 ml) at 80°C for 15 h. Yield of isobutyric acid (**1**) (●), *n*-butyric acid (**2**) (■), and isopropyl trifluoroacetate (**3**) (▲).

The yield of **1** increases sharply with increasing pressure of CO until 30 bar where the maximum yield is 0.62 mmol but the yield of **2** is the highest (0.34 mmol) at 70 atm of CO. Further increasing the CO pressure beyond 30 atm resulted in a lower yield of **1**. In the case of **3**, the yield decreases continuously with increasing CO pressure. Under an atmosphere of CO, the alkyl radical formed in the reaction mixture is supposed to react with CO to form the C–C bond which gives the acid products in this reaction (22–25). Under a low pressure of CO, it would be difficult to form the C–C bond; thus, the yields of **1** and **2** in this reaction are low under that condition. Furthermore, under a high pressure of CO, the oxidation process may become difficult. Therefore, the esterification reaction becomes slower at a high pressure of CO. For maintaining the best concentration of CO in the reaction mixture to facilitate the formation of the C–C bond, the following reactions were carried out under 30 atm of CO pressure.

Effect of the Amount of TFA

Figure 4 demonstrates the effect of the amount of TFA on the yield of the reaction of propane with CO in the presence of $K_2S_2O_8$. In the reaction at least 2 ml of TFA was used. It can be seen that the yields of all the products increase with increasing the amount of TFA up to 5–6 ml, where the maximum yields of **1**, **2**, and **3** are 0.65, 0.31, and 0.40 mmol, respectively. The yields then decrease suddenly with increasing amount of TFA. The concentrations of catalyst and oxidant play a very important role and are controlled by the amount of TFA added. The higher amount of TFA dilutes the reaction mixture and decreases the yield. Considering the results of these experiments it can be concluded that 5 ml of TFA is the optimum amount for this reaction.

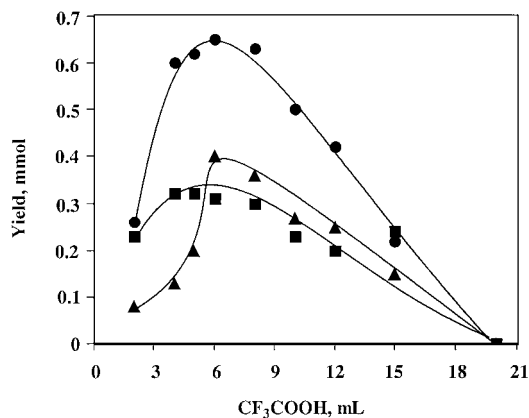


FIG. 4. Effect of the amount of CF_3COOH on the yields of $CaCl_2$ (0.5 mmol)-catalyzed carboxylation reaction of propane (6 bar, 0.98–4.54 mmol) with CO (30 bar) in the presence of $K_2S_2O_8$ (5 mmol) at 80°C for 15 h. Yield of isobutyric acid (**1**) (●), *n*-butyric acid (**2**) (■), and isopropyl trifluoroacetate (**3**) (▲).

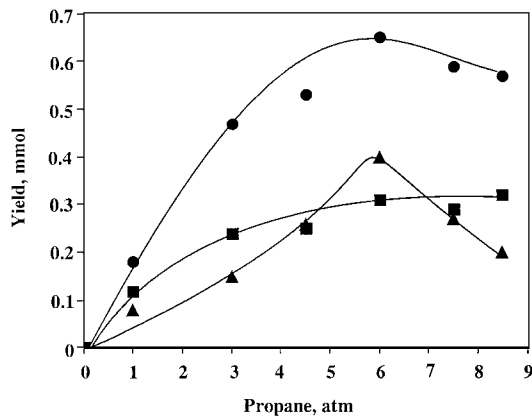


FIG. 5. Effect of the pressure of propane on its carboxylation reaction with CO (30 bar) catalyzed by $CaCl_2$ (0.5 mmol) in the presence of $K_2S_2O_8$ (5 mmol) and CF_3COOH (5 ml) at 80°C for 15 h. Yield of isobutyric acid (**1**) (●), *n*-butyric acid (**2**) (■), and isopropyl trifluoroacetate (**3**) (▲).

Effect of Pressure of Propane

A high concentration of propane in the solution phase facilitates the formation of a C–C bond rather than a C–O bond. Thus, the yields of acid products **1** and **2** continue to increase up to 6 bar of propane pressure (Fig. 5). Increasing pressure of propane beyond 6 bar results in decreasing yields. Here it is thought that the reaction proceeds through the formation of propyl radicals which are generated by the abstraction of a hydrogen atom from propane by calcium oxy radicals ($Ca-O^{\bullet}$). A high concentration of propane may cause the formation of a large excess of propyl radical which may be terminated by further reacting with $Ca-O^{\bullet}$ radicals. However, the yield of product **3** gradually increases with increasing propane pressure. It may be that the consumed propoxide ion releases alcohol upon reaction with TFA. The alcohol ultimately transforms to the ester after reaction with another TFA molecule.

Once again, an atmospheric pressure of propane gives about 95% total yield based on propane. The yield% based on propane continuously decreases with increasing pressure of propane. Since the amount of unreacted propane increases with increasing pressure of propane in the autoclave, the yield based on propane decreases. From these results it can be concluded that the reaction should be carried out under 1–2 bar of propane for high yields of products.

Effect of the Amount of $CaCl_2$

The variation of the yields as a function of the amount of $CaCl_2$ is depicted in Fig. 6. In the absence of catalyst, propane reacted slightly, giving 0.02, 0.01, and 0.12 mmol of **1**, **2**, and **3**, respectively. Addition of the catalyst remarkably increased the yields. However, a low amount of catalyst (0.05 mmol) does not result in a good yield of the products.

As the amount of catalyst increased, the yield dramatically increased up to 0.5 mmol where the highest yields

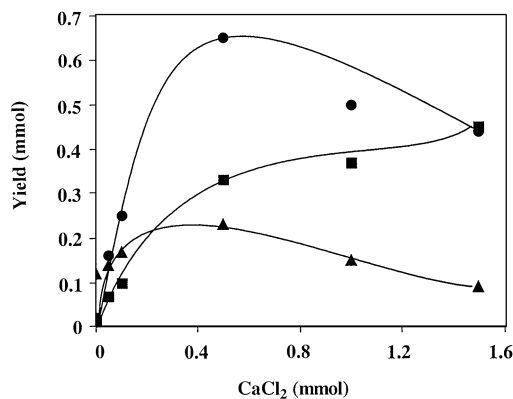


FIG. 6. Effect of the amount of CaCl_2 on the carboxylation reaction of propane (8 bar, 6.06 mmol) with CO (30 bar) in the presence of $\text{K}_2\text{S}_2\text{O}_8$ (5 mmol) in CF_3COOH (5 ml) at 80°C for 15 h. Yield of isobutyric acid (1) (●), *n*-butyric acid (2) (■), and isopropyl trifluoroacetate (3) (▲).

are 0.65, 0.33, and 0.23 mmol of **1**, **2**, and **3**, respectively. After that the yield of **1** gradually decreases with increasing amount of catalyst whereas under the same conditions the yield of **2** gradually increases with increasing amount of catalyst and finally, **2** became the major product when 1.5 mmol of catalyst was used; however, the reason is not clear at present. On the other hand, the yield of **3** decreases with increasing amount of catalyst beyond 0.5 mmol of CaCl_2 .

This figure also indicates that the overall amount of **1** + **2** + **3** decreases with increasing amount of CaCl_2 beyond 0.5 mmol. The decreasing trend in the yield of the total products is due to the decomposition of the products which is observed experimentally in the presence of a large excess of CaCl_2 .

Time Course

Figure 7 demonstrates the effect of reaction time on the yields based on propane and turnover number based on calcium atom under various conditions. The most important aspect of the reaction conditions has been noticed in the time course of the reaction. It is apparent from this figure that no reaction product is observed within 2 h under any reaction conditions. All the products were first observed after 2 h induction period which can be correlated with the formation of the catalytic CaO^{\bullet} radical species.

Plots a and b of this figure demonstrate the total yield (based on propane) and turnover number (based on Ca atom), respectively, as a function of time of the reaction of propane (6 bar) with CO (30 bar) in the presence of CaCl_2 (0.02 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (5 mmol), and TFA (5 ml). It can be seen that the yield% and turnover number of the catalyst gradually increase with time up to 40 h. The highest turnover number obtained is 26.5 (based on Ca) where the yield is 11.7% (based on propane). A prolonged reaction time beyond 40 h resulted in lower results; this may be due

to the rate of the thermal or catalytic decomposition of the products being higher than the rate of the formation.

The variation in the total yield as a function of time of the reaction of propane (6 atm) with CO (30 atm) in the presence of CaCl_2 (0.5 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (5 mmol), and TFA (5 ml) at 80°C is shown in plot c. As the reaction time increases, the yield gradually increases up to 35 h to the maximum value of 33.9%. On the other hand, the reaction gives as high as about 95% total yield when 1 atm of propane is used for 24 h (curve d) under the same reaction conditions as those described for curve c. A reaction time longer than 24 h resulted in the lower yield, maybe for the same reasons as those described above.

Reaction of Various Saturated Hydrocarbons with CO

The carboxylation reaction of various saturated hydrocarbons such as ethane, cyclopentane, cyclohexane, cycloheptane, and cyclooctane was carried out using the optimum conditions for the reaction of propane: CO (30 bar), CaCl_2 (0.5 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (5 mmol), and TFA (5 ml) at 80°C . Table 2 presents the results of this experiments. Ethane also undergoes the carboxylation reaction with CO efficiently, giving as high as 88% total yield. In this case about 23% of acetic acid is formed in place of ester. Of the cycloalkanes used in this reaction, cyclopentane and cyclohexane undergo the reaction remarkably, giving about 44 and 33% total yields, respectively. In the case of cyclopentane, cyclopentanecarboxylic acid is the main product but in the case of cyclohexane the ester is the main one. On the other hand, cycloheptane gives less remarkable yields where ester is the dominant product. However, cyclooctane did not react with CaCl_2 catalyst in the presence of $\text{K}_2\text{S}_2\text{O}_8$ and TFA. Thus, it is apparent that the CaCl_2 catalyst is more

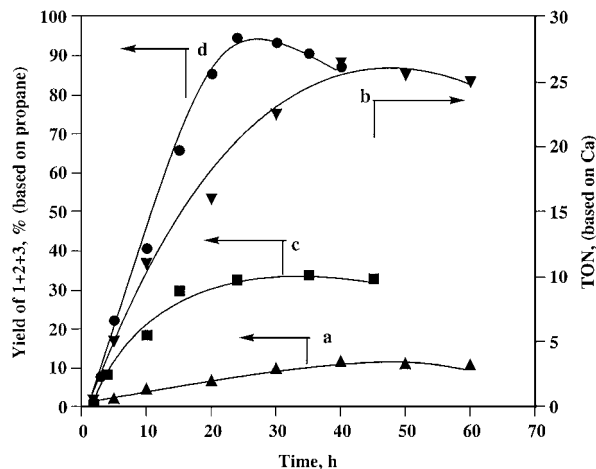


FIG. 7. Time course of the carboxylation reaction of propane with CO using 5 ml of TFA at 80°C . Conditions: (a and b) Propane (6 bar, 4.54 mmol), CO (30 bar), CaCl_2 (0.02 mmol), and $\text{K}_2\text{S}_2\text{O}_8$ (5 mmol); (c) propane (6 bar), CO (30 bar), CaCl_2 (0.5 mmol), and $\text{K}_2\text{S}_2\text{O}_8$ (5 mmol); (d) propane (1 bar), CO (30 bar), CaCl_2 (0.5 mmol), and $\text{K}_2\text{S}_2\text{O}_8$ (5 mmol).

TABLE 2

Reaction of Various Saturated Hydrocarbons with CO

$$\text{R-H} + \text{CO} \xrightarrow[\text{K}_2\text{S}_2\text{O}_8, 80^\circ\text{C}]{\text{CaCl}_2} \underset{\text{acid}}{\text{R-COOH}} + \underset{\text{ester}}{\text{R-O-COCF}_3}$$

Entry	Substrate	Product (mmol) ^a		Yield (%) ^b
		acid	ester	
1	C ₂ H ₆ ^c	0.51	— ^d	88
2	C ₃ H ₈	<i>iso</i> , 0.34 <i>n</i> , 0.18	0.20	95
3	<i>c</i> -C ₅ H ₁₀	0.31	0.13	44
4	<i>c</i> -C ₆ H ₁₂	0.15	0.18	33
5	<i>c</i> -C ₇ H ₁₄	0.05	0.07	12
6	<i>c</i> -C ₈ H ₁₆	—	—	—

Reaction conditions: 25-ml autoclave, ethane, propane (1 bar, 0.76 mmol), other hydrocarbons (1 mmol), CO (30 bar), CaCl₂ (0.5 mmol), K₂S₂O₈ (5 mmol), TFA (5 ml), 80°C, 24 h.

^a Determined by GC.

^b Based on hydrocarbon.

^c Reaction time 48 h.

^d Acetic acid (0.16 mmol) was also formed.

efficient for functionalization of lower alkanes rather than cycloalkanes.

The activation parameters for the reaction of propane (5 bar) with CO (30 bar) catalyzed by CaCl₂ (0.5 mmol) in the presence of K₂S₂O₈ (5 mmol) and TFA (5 ml) within the temperature range of 343 and 358 K for the formation of isobutyric and *n*-butyric acids and isopropyl trifluoroacetate have been determined by Arrhenius and Eyring equations. Figure 8 shows the Arrhenius plots e, f, and g for

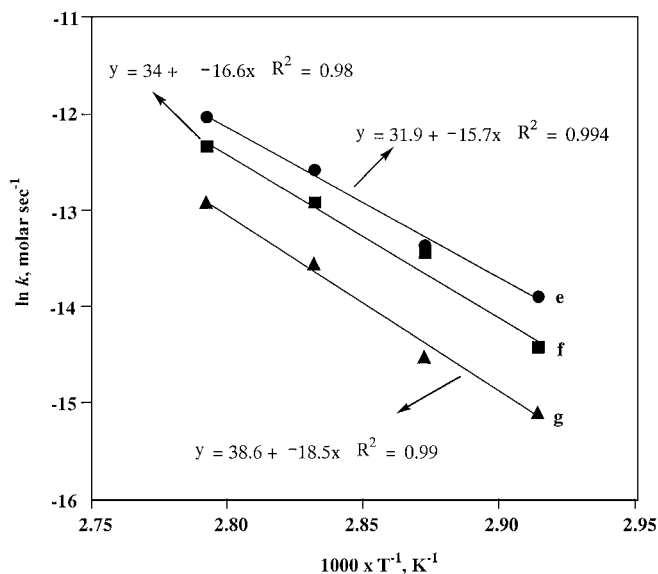


FIG. 8. Arrhenius plots for the products **1**, **2**, and **3**. Energies of activation for the products of **1**, **2**, and **3** are 130.3, 138.0, and 153.8 kJ/mol, respectively, and frequency factors are 7.14×10^{13} , 5.83×10^{14} , and $5.80 \times 10^{16} \text{ s}^{-1}$, respectively. Conditions: propane (5 bar), CO (30 bar), CaCl₂ (0.5 mmol), K₂S₂O₈ (5 mmol), and TFA (5 ml) at 70–85°C.

the products of **1**, **2**, and **3**. The energies of activation (E_a) for the formation of **1**, **2**, and **3** have been determined from the slopes of the plots to be 130.3, 138.0, and 153.8 kJ/mol, respectively. In each case the energy of activation is sufficient for breaking the bond in the transition state and quite comparable with the activation energy for the formation of methyl radical in the Li/MgO-catalyzed oxidative coupling of methane (22). The frequency factors (A) have also been determined from the intercept of the plots to be 7.14×10^{13} , 5.83×10^{14} , and $5.80 \times 10^{16} \text{ s}^{-1}$, respectively.

The activation enthalpy (ΔH^\ddagger), activation entropy (ΔS^\ddagger), and activation free energy (ΔG_{353}^\ddagger) for the formation of **1**, **2**, and **3** from the reaction of propane (5 bar) with CO (30 bar) using the same reaction conditions as those described above have been determined by Eyring plots (Fig. 9). The activation enthalpies were calculated for the formation of the products **1**, **2**, and **3** from the slopes of the plots h, i, and j to be 128.0, 134.7, and 150.5 kJ/mol, respectively. In each case the enthalpy of activation is sufficient for breaking the bond in the transition state. The entropies of activation which were derived from the intercepts of the plots are 10.3, 28.6, and 66.8 J/mol K, respectively. The activation free energies are also calculated to be 124.4, 123.9, and 126.9 kJ/mol for the products **1**, **2**, and **3**, respectively. The activation parameters for the formation of **1** are very close to those for **2** but differ from those for the formation of **3** which reveals that two reactions proceed in the two different pathways.

Although the mechanism of the functionalization of saturated hydrocarbons to carboxylic acids and alkyl

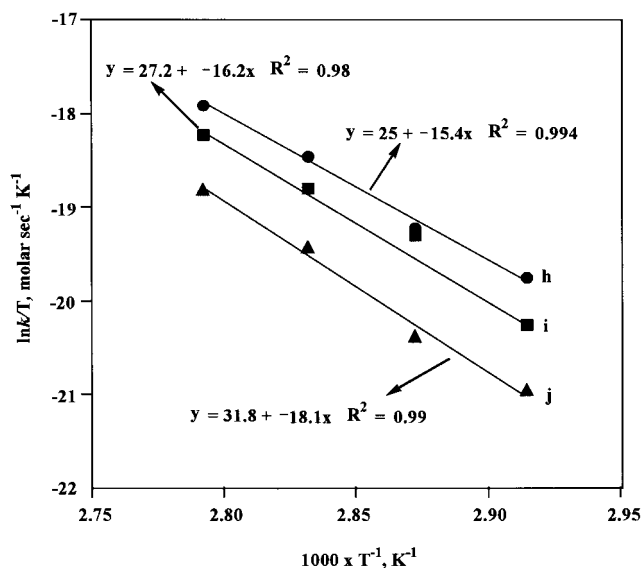


FIG. 9. Eyring plots for the products of **1**, **2**, and **3**. The thermodynamic terms ΔH^\ddagger , ΔS^\ddagger , and ΔG_{353}^\ddagger are determined to be $\Delta H^\ddagger = 128.0$, 134.7, and 150.5 kJ/mol; $\Delta S^\ddagger = 10.3$, 28.6, and 66.8 J/mol K; and $\Delta G_{353}^\ddagger = 124.4$, 123.9, and 126.9 kJ/mol, respectively. Conditions: propane (5 bar), CO (30 bar), CaCl₂ (0.5 mmol), K₂S₂O₈ (5 mmol), and TFA (5 ml) at 70–85°C.

trifluoroacetates catalyzed by CaCl_2 in the presence of $\text{K}_2\text{S}_2\text{O}_8$ in TFA at 80°C is unclear, we believe that the reaction involves hydrogen atom abstraction from the alkane by radicals such as calcium oxy radicals (Ca-O^\bullet) or radical-like species to generate the corresponding alkyl radicals. The generated alkyl radicals react with CO to give acyl radicals (R-CO^\bullet). The acyl radical then reacts with Ca-O^\bullet to form a complex from which the acyl cation transfers to a TFA molecule to form a mixed anhydride. It has been reported that this type of mixed anhydride reacts further with TFA to form carboxylic acid and trifluoroacetic anhydride (23, 24). The role of $\text{K}_2\text{S}_2\text{O}_8$ is to reoxidize the $-\text{CaOH}$ catalyst to $-\text{CaO}^\bullet$. Finally, $\text{K}_2\text{S}_2\text{O}_8$ is transformed to KHSO_4 which is confirmed by IR spectra of the solid phase after completion of the reaction. Alkyl radicals (R^\bullet) actually react very fast with CO to form the acyl radicals (25–30). The ester products **3** formed in the reaction mixture may be formed in a different way.

The IR studies of the solid sample which was prepared by the reaction of CaCl_2 with TFA under a nitrogen atmosphere reveal that the CaCl_2 first reacts with TFA to form $\text{Ca}(\text{CF}_3\text{COO})_2$. It is assumed that in the final reaction mixture, $\text{Ca}(\text{CF}_3\text{COO})_2$ successively reacts with $\text{K}_2\text{S}_2\text{O}_8$ and CO to form calcium peroxide which then converts to the active species Ca-O^\bullet radical. The sufficient activation energies and enthalpies for the formation of **1**, **2** and **3** indicate that the reaction is endothermic and controlled by external heat.

SUMMARY AND CONCLUSIONS

Calcium dichloride has been found to be an efficient catalyst for the reaction of lower alkanes such as ethane, propane, cyclopentane, and cyclohexane with CO to afford the corresponding carboxylic acids. The reaction conditions were optimized for the reaction of propane with CO. Propane gave about 95% total yield (based on propane) of **1**, **2**, and **3** when 1 bar of propane reacted with 30 bar of CO in the presence of CaCl_2 (0.5 mmol), $\text{K}_2\text{S}_2\text{O}_8$ (5 mmol), and TFA (5 ml) at 80°C for 24 h. In this reaction **1** is formed as the main product and **2** and **3** are formed as by-products. Using the optimum reaction conditions for propane, we attempted the reaction of several saturated hydrocarbons with CO. Ethane gave about 88% total yield; however, in this case 23% acetic acid was formed by the oxidation of ethane. The ester product of the reaction of ethane was not detected by GC. Of the cycloalkanes used in this reaction, cyclopentane and cyclohexane undergo the reaction remarkably, giving about 44 and 33% total yields, respectively. In the case of cyclopentane, acid is the main product but in the case of cyclohexane the ester is the main one. On the other hand, cycloheptane gives less remarkable yields where ester is the dominant product. Cyclooctane did not react.

The activation parameters for the reaction of propane (5 bar) with CO (30 bar) catalyzed by CaCl_2 (0.5 mmol) in the presence of $\text{K}_2\text{S}_2\text{O}_8$ (5 mmol) and TFA (5 ml) within the

temperature range of 343 and 358 K for the formation of **1**, **2**, and **3** have been determined by Arrhenius and Eyring equations to be $E_a = 130.3$, 138.0 , and 153.8 kJ/mol; $A = 7.14 \times 10^{13}$, 5.83×10^{14} , and 5.80×10^{16} s^{-1} ; $\Delta H^\ddagger = 128.0$, 134.7 , and 150.5 kJ/mol; $\Delta S^\ddagger = 10.3$, 28.6 , and 66.8 J/mol K; and $\Delta G_{353}^\ddagger = 124.4$, 123.9 , and 126.9 kJ/mol for the products **1**, **2**, and **3**, respectively. Since the reaction of lower alkanes gives very high yields and uses a cheap catalyst, it has importance from the industrial point of view.

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