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Transformation of propane and CO to carboxylic acid and ester by highly active $CaCl_2$ catalyst

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The functionalization reaction of propane with CO to afford carboxylic acids and an ester by $CaCl_2$ catalyst in the presence of $K_2S_2O_8$ and CF_3COOH has been studied. The reaction gave isobutyric acid as the main product and n-butyric acid and isopropyl trifluoroacetate as by-products. Atmospheric pressure of propane underwent the reaction with 30 atm of CO pressure at 80 °C for 24 h, giving about 95% total yield based on propane. The activation and thermodynamic parameters have been determined 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} 1/s; $\Delta H^{\ddagger} = 128.0$, 134.7 and 150.5 kJ/mol; $\Delta S^{\ddagger} = 10.3$, 28.6 and 66.8 J/mol K and $\Delta G^{\ddagger}_{253} = 124.4$, 123.9 and 126.9 kJ/mol for the products of isobutyric acid, n-butyric acid and isopropyl trifluoroacetate, respectively.

Keywords: saturated hydrocarbons, propane, carbon monoxide, calcium dichloride, carboxylic acid, catalysis

1. Introduction

Propane is one of the abundantly available saturated hydrocarbons on the world, being utilized mainly as a clean burning fuel for energy supply. Thus, the direct and selective functionalization of propane to useful 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 low reactivity of propane and poor selectivity of its products make the process inconvenient for industrial use. Various types of researches on propane transformation have been reported within the last few decades such as oxidative dehydrogenation of propane to propene [3–7], oxidation of propane to alcohol [8,9] or acrylic acid [10–12], carbonylation of propane with CO to butanal [13], ammoxidation 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 propanes [17].

Direct carboxylation of propane with CO to carboxylic acids is an important functionalization process; however, much less examples of this reaction are reported [18]. Recently, we found that Mg powder [19,20] promotes the carboxylation of propane; however, the reaction is not catalytic and gives low yield. In this paper, we describe the high yield functionalization of propane to isobutyric acid (**1**), n-butyric acid (**2**) and isopropyl trifluoroacetate (**3**) by a highly efficient and cheap, $CaCl_2$ catalyst in the presence of $K_2S_2O_8$ and CF_3COOH (TFA).

2. Experimental

2.1. Procedure of the carboxylation reaction of propane

The catalyst and $K_2S_2O_8$ were placed in a 25 ml stainless-steel autoclave equipped with a Teflon-coated magnetic stirring bar (12 mm, octagonal). Then 5 ml of TFA was introduced into the autoclave. Then the autoclave was closed and flushed with propane three times for replacing the air inside the autoclave and then pressurized with the desired pressures of propane and CO. Then the autoclave was heated with stirring at a fixed temperature for the desired length of time. After finishing the reaction, 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 added to the reaction mixture and stirred for 5 min. The contents of the carboxylic acids were analyzed by gas chromatography using a Shimadzu GC-8A equipped with a flame ionization detector by using a 3 m × 3.0 mm i.d. stainless-steel column packed with Unisole $10T + H_3PO_4$ $(5 + 0.5)\%$ on 80/100 mesh Uniport HP at an injection/detection temperature of 220 °C and at a column temperature of 130 °C. The ester product of propane was characterized by NMR spectroscopy.

3. Results and discussion

3.1. Effect of alkaline earth compounds on the carboxylation reaction of propane

Although the functionalization of propane is difficult due to its low activity, various types of promoter or catalyst systems can easily functionalize propane to functionalized

Table 1
Effect of alkaline earth compounds on the carboxylation reaction of propane with CO.[a]

Entry	Catalyst	Yield[b] (mmol)			Yield (**1** + **2** + **3**)[c] (%)	TON[d]
		1	**2**	**3**		
1	None	0.02	0.01	0.12	3.3	–
2	$CaCl_2 \cdot 2H_2O$	0.62	0.31	0.20	25.0	2.26
3	CaO	0.54	0.19	0.19	20.3	1.84
4	CaO_3	0.46	0.16	0.12	16.3	1.48
5	$Ca(OAc)_2 \cdot 2H_2O$	0.31	0.11	0.10	11.5	1.04
6	$Ca(acac)_2 \cdot 2H_2O$	0.10	0.04	0.05	4.2	0.38
7	$Ca(OH)_2$	0.01	0.01	0.04	1.3	0.12
8	$CaSO_4 \cdot 2H_2O$	Trace	–	0.15	3.3	0.30
9	Mg[e]	0.35	0.16	0.02	10.6	0.11
10	$MgCl_2$	Trace	–	Trace	–	–
11	$BaCl_2$	Trace	Trace	Trace	–	–

[a] Conditions: autoclave (25 ml), propane (6 atm, 4.54 mmol), CO (30 atm), alkaline earth compound (0.5 mmol), $K_2S_2O_8$ (4 mmol) and TFA (5 ml) at 80 °C for 15 h.

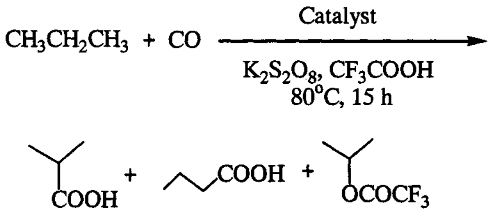
[b] Determined by GC.

[c] Based on propane.

[d] Turnover number = moles of total products/moles of Ca.

[e] Mg (5 mmol), TFA (3 ml), 30 h.

products [8–17]. We discovered that Mg powder is a very active promoter for carboxylation of propane with CO to iso- and n-butyric acids. This result encouraged us to investigate an active catalyst from alkaline earth compounds. Thus, in this work first we investigated the catalytic performance of alkaline earth compounds for the carboxylation reaction of propane with CO in the presence of $K_2S_2O_8$ and TFA at 80 °C for 15 h in a 25 ml stainless-steel autoclave. The isobutyric acid (**1**) was formed in this reaction as a main product and n-butyric acid and isopropyl trifluoroacetate were formed as by-products (equation (1)). Table 1 demonstrates the results of this reaction.



(1)

1 **2** **3**

In the absence of catalyst the reaction proceeded in very low yields of **1**, **2** and **3** (0.02, 0.01 and 0.12 mmol, respectively, entry 1). The results of entries 2–5 in table 1 indicate that the combination of Ca-compounds with $K_2S_2O_8$ under the same reaction conditions makes good systems for this reaction of propane.

It is apparent from these results that $CaCl_2$ (entry 2) 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 atom. The $CaSO_4$ (entry 8) and other metal compounds, $MgCl_2$ (entry 10) and $BaCl_2$ (entry 11) did not bring about the reaction of propane with CO. Although the reaction of Mg powder gives a remarkable result (entry 9), it is not catalytic.

3.2. Optimization of $CaCl_2$-catalyzed carboxylation of propane

Since $CaCl_2$ catalyzes the carboxylation reaction of propane with CO, our next concern is to optimize the reaction conditions. The optimized conditions of the reaction are summarized in table 2. Experiments were conducted to gain insight into the reaction conditions that would favor the formation of **1** from propane and CO. As can be seen from entry 1 of table 2, propane underwent the reaction at as low as 25 °C in low yields. Increasing the temperature brings an increase of the quantities of **1**, **2** and **3**. The highest yield of **1** is attained at 80 °C (entry 3). Then the yields of **1** and **2** decrease at higher temperature beyond 80 °C; however, the yield of **3** increases unexpectedly with increasing temperature beyond 85 °C. The thermal or catalytic decomposition of acid products at high temperature to the smaller molecular products may be the cause of the decreasing trend of the products. To investigate this phenomenon a control experiment was carried out where a mixture of pure **1**, **2** and **3** (1 mmol of each) was heated in the mixture of $CaCl_2$ (0.5 mmol), $K_2S_2O_8$ (5 mmol) and TFA (5 ml) under nitrogen atmosphere (5 atm) at 90 °C for 15 h. Then the reaction was analyzed by GC and NMR which gave 0.70, 0.87 and 0.95 mmol of **1**, **2** and **3**, respectively. GC and NMR charts also showed several small peaks which were actually difficult to interpret. Moreover, the gas-phase analysis showed the presence of CO_2 gas. Thus, it can be concluded that the lower yields of **1** and **2** of the carboxylation of propane at 90 °C are to be attributed to their decomposition under the reaction conditions (entry 5). Moreover, the solubility of CO decreases with increasing temperature. Thus, the carboxylation reaction may become slow due to the low concentration of CO in the solution.

In the absence of CO the reaction did not give **1** and **2** but afforded 0.65 mmol of **3** (entry 6). Under the at-

Table 2
Effect of reaction conditions on the carboxylation reaction of propane with CO.[a]

Entry	T (°C)	CO (atm)	TFA (ml)	Propane (atm)	$CaCl_2$ (mmol)	Yield[b] (mmol)			Yield ($\mathbf{1}+\mathbf{2}+\mathbf{3}$)[c] (%)
						1	**2**	**3**	
1	25	30	5	6	0.5	0.08	0.02	Trace	2.0
2	60	30	5	6	0.5	0.10	0.04	Trace	3.0
3	80	30	5	6	0.5	0.62	0.31	0.20	25.0
4	85	30	5	6	0.5	0.60	0.30	0.24	25.1
5	90	30	5	6	0.5	0.50	0.28	0.37	25.3
6	80	0	5	6	0.5	–	–	0.65	14.3
7	80	1	5	6	0.5	0.09	0.13	0.63	18.7
8	80	40	5	6	0.5	0.60	0.30	0.14	22.9
9	80	30	2	6	0.5	0.26	0.23	0.08	12.6
10	80	30	6	6	0.5	0.65	0.31	0.40	30.0
11	80	30	10	6	0.5	0.50	0.23	0.27	22.0
12	80	30	5	1	0.5	0.18	0.12	0.08	51.0
13	80	30	5	1[d]	0.5	0.34	0.18	0.20	95.0
14	80	30	5	8.5	0.5	0.57	0.32	0.20	17.9
15	80	30	5	6	0.05	0.16	0.07	0.14	6.1
16	80	30	5	6	1	0.50	0.37	0.15	16.8

[a] Conditions: autoclave (25 ml), $K_2S_2O_8$ (4–5 mmol), 15 h.
[b] Determined by GC.
[c] Based on propane.
[d] Reaction time 24 h.

mospheric pressure of CO, the carboxylation of propane proceeds where the yield of **2** (0.13 mmol) is higher than **1** (0.09 mmol) (entry 7). The increase of CO pressure resulted in the increase of yields of **1** and **2** up to 30 atm, giving the highest yield of **1** (0.62 mmol, entry 3). CO in this system acts as a trapping agent for propyl radicals which are generated in the reaction mixture to form the acyl radicals that give acid products in this reaction [21,22].

The amount of solvent in the reaction mixture gives an important effect on the yield. The reaction rate depends on the concentrations of reactants as well as catalyst, which are controlled by the addition of a proper amount of solvent. In this respect, the optimum amount of solvent for this reaction was determined. The results are summarized in table 2. From these results it can be seen that the reaction took place when at least 2 ml of TFA (entry 9) was used. The yields of all products increase with increasing the amount of TFA upto 6 ml (entry 10), where maximum yields of **1**, **2** and **3** are 0.65, 0.31 and 0.40 mmol, respectively. Then the yields decrease suddenly with increasing the amount of TFA (entry 11). When the amount of TFA less than 5 ml was used, the concentrations of catalyst, oxidant as well as reactant all increased severely so that the reaction probably diverted to the side reactions. On the other hand, the higher amount of solvent dilutes the reaction mixture and decreases the yields. From these results it has been concluded that 5 ml of TFA would be the optimum amount for this reaction because the selectivity to **1** is higher in the case of 5 ml of TFA (entry 3) than in the case of 6 ml of TFA (entry 10).

Atmospheric pressure of propane underwent the reaction, giving 51% total yield based on propane after 15 h reaction time (entry 12). Interestingly enough, the reaction gave about 95% total yield when 1 atm of propane reacted with CO for 24 h (entry 13). The yield% based on propane decreases with increasing propane pressure. Since the amount of unreacted propane increases with increasing the pressure of propane in the autoclave, the yield based on propane decreases. According to these results the reaction should be carried out under low propane pressure (1–2) for high yield based on propane.

In the absence of catalyst, propane underwent the reaction slightly, giving 0.02, 0.01 and 0.12 mmol of **1**, **2** and **3**, respectively. Addition of a lower amount of catalyst than 0.05 mmol did not give any product. As the amount of catalyst increased, the yields dramatically increased upto 0.5 mmol where the highest yields are 0.65, 0.31 and 0.40 mmol of **1**, **2** and **3**, respectively (entry 10). The higher amount of $CaCl_2$ also resulted in low yield of **1** (entry 16) but high yield of **2**. On the other hand, the yield of **3** decreases with increasing the amount of catalyst beyond 0.5 mmol of $CaCl_2$.

The variation of the yields based on propane and turnover number based on Ca atom as a function of time is depicted in figure 1. It is apparent from this figure that no reaction product is observed within 2 h in either reaction condition. All the products first appeared after 2 h reaction time.

Plots (a) and (b) in figure 1 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 atm) with CO (30 atm) in the presence of $CaCl_2$ (0.02 mmol), $K_2S_2O_8$ (5 mmol) and TFA (5 ml). It can be seen from these plots that the yield% and turnover number of the catalyst gradually increase as the time of the reaction goes to 40 h. The highest turnover number is obtained to be 26.5 (based on Ca) where the yield% is 11.7 (based on propane). The prolonged reaction time be-

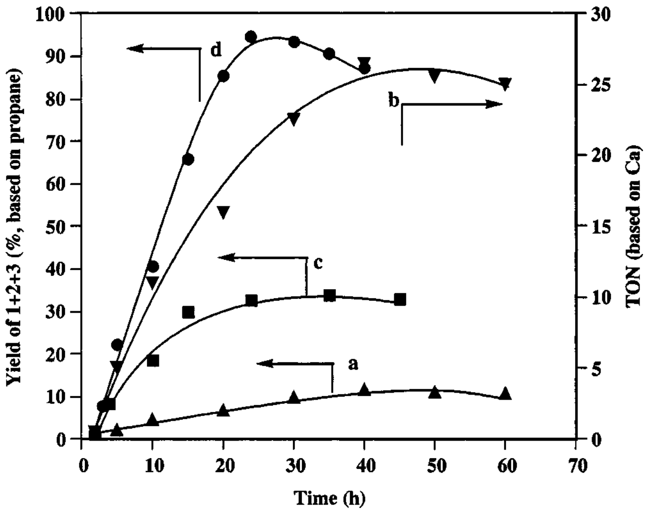


Figure 1. Time course of the carboxylation reaction of propane with CO using 5 ml of TFA at 80 °C. Conditions: for plots (a) and (b) propane (6 atm, 4.54 mmol), CO (30 atm), $CaCl_2$ (0.02 mmol), $K_2S_2O_8$ (5 mmol); for plot (c) propane (6 atm), CO (30 atm), $CaCl_2$ (0.5 mmol), $K_2S_2O_8$ (5 mmol) and for plot (d) propane (1 atm), CO (30 atm), $CaCl_2$ (0.5 mmol), $K_2S_2O_8$ (5 mmol).

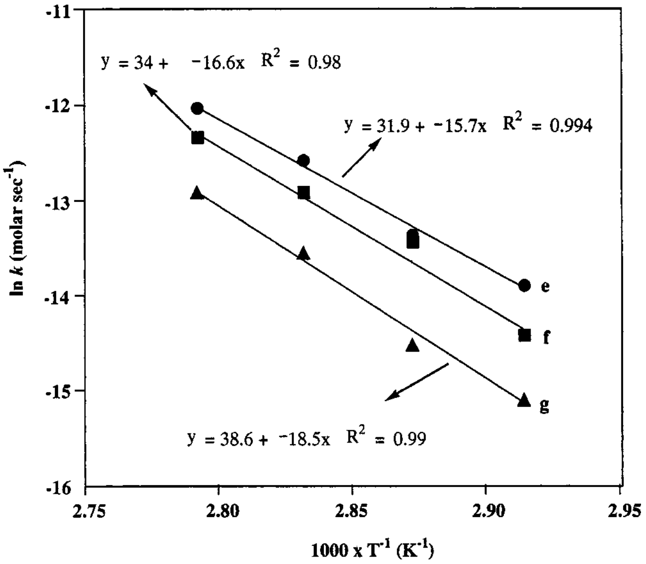


Figure 2. Arrhenius plots for the products **1**, **2** and **3**. Energies of activation and frequency factors for the products **1**, **2** and **3** are 130.3, 138.0 and 153.8 kJ/mol and 7.14×10^{13}, 5.83×10^{14} and 5.80×10^{16} 1/s, respectively. Conditions: propane (5 atm), CO (30 atm), $CaCl_2$ (0.5 mmol), $K_2S_2O_8$ (5 mmol) and TFA (5 ml) within the temperature range 70–85 °C.

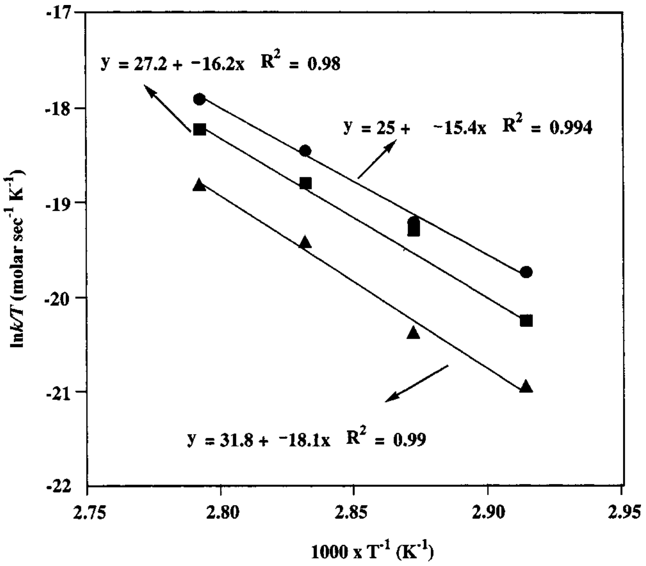


Figure 3. Eyring plots for the products of **1**, **2** and **3**. The thermodynamic terms $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}_{353}$ are $\Delta H^{\ddagger} = 128.0$, 134.7 and 150.5 kJ/mol; $\Delta S^{\ddagger} = 10.3$, 28.6 and 66.8 J/mol K and $\Delta G^{\ddagger}_{353} = 124.4$, 123.9 and 126.9 kJ/mol, respectively. Conditions: propane (5 atm), CO (30 atm), $CaCl_2$ (0.5 mmol), $K_2S_2O_8$ (5 mmol) and TFA (5 ml) within the temperature range 70–85 °C.

yond 40 h resulted in the lower yields may be due to the deactivation of the catalyst.

The variation of 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), $K_2S_2O_8$ (5 mmol) and TFA (5 ml) at 80 °C is shown by plot (c). As the reaction time goes, the yield gradually increases until 35 h to attain the maximum value 33.9%. On the other hand, the reaction gives as high as 95% total yield when 1 atm of propane is used for 24 h (curve (d)) under the same reaction conditions as described for curve (c). In this case almost all of the propane transfers to products. Thus, the longer reaction time than 24 h resulted in the lower yield maybe due to the catalytic decomposition of the products.

The activation parameters E_a and A and the thermodynamic parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ at the activated state for the reaction of propane with CO have been calculated by the Arrhenius and Eyring theories within the temperature range of 243–258 K. Figure 2 shows the Arrhenius plots (e), (f) and (g) for the products of **1**, **2** and **3** from where the apparent activation energies and frequency factors have been calculated to be $E_a = 130.3$, 138.0 and 153.8 kJ/mol and $A = 7.14 \times 10^{13}$, 5.83×10^{14} and 5.80×10^{16} 1/s for the products **1**, **2** and **3**, respectively. These values are quite reasonable for the abstraction of hydrogen from propane and comparable with the oxidation of methane by $CuCl_2$ and K_2PdCl_4 mixed catalyst to methanol [23]. Figure 3 shows the Eyring plots (h), (i) and (j) for the products **1**, **2** and **3**, respectively. From the Eyring plots the thermodynamic terms $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}$ have been calculated 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 $\Delta G^{\ddagger}_{253} = 124.4$, 123.9 and 126.9 kJ/mol for the products **1**, **2** and **3**, respectively. In each case the activation enthalpy is sufficient for breaking the bond in the transition state. The lower $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for **1** than **2** and **3** suggests a greater degree of bond-forming in the transition state in the case of **1**, compared with that of **2** and **3**.

Although the mechanistic details of the reaction are not clear yet, it is believed that the reaction involves hydrogen atom abstraction from alkane by a radical such as a calcium oxy radical (–Ca–O·) or a radical like species to generate the corresponding alkyl radical which could react with CO to give an acyl radical (R–CO$^{\cdot}$) [24,25]. Then the acyl radical reacts with –Ca–O$^{\cdot}$ to form a complex (–CaO–OCR) from which R–CO^{+} would be released [22] and reacts with TFA to form a mixed anhydride RCO–O–COCF$_3$ [26] which would react further with TFA to form acid products **1** and **2** and a homogeneous anhydride (CF$_3$CO)$_2$O [27]. The ester products **3** in the reaction mixture may be formed in a different way. The linearity of the curves of figures 2 and 3 and the rather high values of E_a and $\Delta H^{\ddagger}$ for all products reveal that the C–H bond breaking step at the transition state may be the rate-limiting step. The details of the mechanism are under investigation.

4. Summary and conclusions

Calcium dichloride has been found to be an effective catalyst for the carboxylation reaction of propane with CO in the presence of K$_2$S$_2$O$_8$ and TFA. In this reaction, propane gave about 95% total yield (based on propane) of **1**, **2** and **3** when 1 atm of propane reacted with 30 atm of CO in the presence of CaCl$_2$ (0.5 mmol), K$_2$S$_2$O$_8$ (5 mmol) and TFA (5 ml) at 80 °C for 24 h. The reaction gave **1** as a major product and **2** and **3** as by-products. However, in the case of 1 atm of CO pressure and a higher amount of catalyst than 0.5 mmol, the reaction favors formation of **2**. The activation and the thermodynamic parameters for the formation of **1**, **2** and **3** from the reaction of propane with CO within the temperature range of 243–258 K have been determined. The apparent activation energies and frequency factors are 130.3, 138.0 and 153.8 kJ/mol and 7.14×10^{13}, 5.83×10^{14} and 5.80×10^{16} 1/s for **1**, **2** and **3**, respectively. The thermodynamic terms $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}_{253}$ have been determined to be 128.0, 134.7 and 150.5 kJ/mol; 10.3, 28.6 and 66.8 J/mol K and 124.4, 123.9 and 126.9 kJ/mol for **1**, **2** and **3**, respectively. Since the present reaction of propane gives very high yields and provides a cheap catalyst, it is of importance in the industrial point of view.

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