Pergamon

Tetrahedron Letters 40 (1999) 8867–8871

TETRAHEDRON
LETTERS

Cobalt catalyzed carboxylation reaction of saturated hydrocarbons with CO in the presence of $K_2S_2O_8$ and TFA under mild conditions

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Received 30 August 1999; revised 20 September 1999; accepted 24 September 1999

Abstract

Cobalt(II) acetate ($Co(OAc)_2$) has been found to be an efficient catalyst for the carboxylation reaction of saturated hydrocarbons with CO to yield the corresponding carboxylic acids in high yields in the presence of $K_2S_2O_8$ and CF_3COOH. About 89.5% conversion of propane is obtained in this reaction. The activation parameters of the reaction of propane have been determined by Arrhenius and Eyring plots. © 1999 Elsevier Science Ltd. All rights reserved.

Transformation of saturated hydrocarbons into their corresponding functionalized products has been of great interest in recent times due to their abundant resources. However, it is challenging to discover the economically feasible and selectively transferable processes due to the lower reactivity of the saturated hydrocarbons than their functionalized products.[1] The carboxylation reaction of saturated hydrocarbons with CO to afford the corresponding carboxylic acids is one of the most important functionalization processes, however, much less is known about this reaction. Carboxylation of lower alkanes and cycloalkanes[2,3] catalyzed by transition metals and super acids[4] gives low yields of corresponding acids. Recently, we have found that the $VO(acac)_2$ catalyst efficiently converts methane and CO to acetic acid.[5] In continuing studies on the activation of alkanes by transition metals, we have found that $Co(OAc)_2$ is an efficient catalyst for the reaction of saturated hydrocarbons especially propane with CO. In this communication, we would like to describe the high yield carboxylation reaction of saturated hydrocarbons with CO catalyzed by $Co(OAc)_2$ in the presence of $K_2S_2O_8$ in trifluoroacetic acid (TFA).

The screening of catalysts has been carried out initially using propane as a substrate to find out the active catalyst system for this reaction of saturated hydrocarbons as shown in Scheme 1. The results are demonstrated in Table 1.

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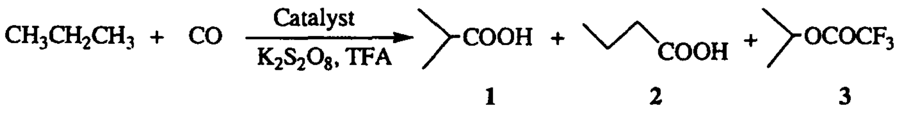
PII: S0040-4039(99)01863-8



Scheme 1.

Table 1
Effect of catalysts on the carboxylation reaction of propane[a]

Entry	Catalyst	Yield (mmol)[b]			Yield (%)[c]
		1	2	3	
1	none	0.01	0.01	0.02	0.4
2	$Co(OAc)_2$	0.43	0.13	0.35	12.3
3	$VO(acac)_2$[d]	0.57	0.30	0.49	19.2
4	$Co(OAc)_2$[e]	trace	trace	--	--
5	$CoCl_2$	0.11	0.06	0.07	3.7
6	Co_3O_4	0.05	0.02	0.04	1.5
7	$Mn(OAc)_2$	0.04	0.02	--	1.3
8	$Ru(acac)_3$	0.01	0.02	--	0.7
9	$IrCl_3$	trace	--	--	--

[a] Conditions: Catalyst (0.1 mmol), propane (6 atm, 4.54 mmol), CO (40 atm), $K_2S_2O_8$ (5 mmol) and TFA (5 mL) at 80 °C for 15 h. [b] Determined by GC. [c] Based on propane. [d] Acetic acid (0.23 mmol) and acetone (0.12 mmol) were formed. [e] Reaction without $K_2S_2O_8$.

The reaction of propane hardly proceeded when $K_2S_2O_8$ and $Co(OAc)_2$ were used separately, giving very low (entry 1) and trace (entry 4) yields. The combination of $Co(OAc)_2$ or $VO(acac)_2$ and $K_2S_2O_8$ under the same reaction conditions gave remarkably high yields (12.3 and 19.2% yields of acids based on propane) (entries 2 and 3).[6] Although $VO(acac)_2$ is a highly active catalyst for the carboxylation of methane,[5] it gives a more complex reaction mixture for the carboxylation of propane, resulting in lower selectivity for the main product (**1**). $CoCl_2$ also catalyzed the reaction in low yields (entry 5). The metal compounds of entries 6, 7, and 8 promoted this reaction slightly whereas $IrCl_3$ (entry 9) did not work significantly in this reaction. Considering the selectivity and yield, it is apparent that the $Co(OAc)_2$ is a significantly good catalyst in the carboxylation reaction of propane. The results of the reaction of propane under various conditions are summarized in Table 2. From this Table it can be seen that the yields of products **1**, **2** and **3** substantially increase as the reaction temperature increases and attain the maximum values of **1** and **2** (0.44 and 0.13 mmol, respectively) at 70°C (entry 2) and **3** (0.35 mmol) at 80°C (entry 3). The yield of the product **1** decreases at high temperatures beyond 70°C. The decreasing trend may be due to the thermal or catalytic decomposition of acid products or the lower solubility of the educts propane and CO at high temperature. It is obvious that 70°C is the convenient temperature for the formation of acid products which are the main target of this work. Therefore, the following reactions were carried out at the optimum temperature of 70°C.

In this reaction, carbon monoxide acts not only as a carbonyl source but also as a reducing agent. Both of these properties of carbon monoxide increase with increasing pressure where the C–C bond would form dominantly. In fact, this reaction proceeded in low yields of **1** and **2** but high yield of **3** under low pressure of carbon monoxide such as under 1 atm of CO pressure (entry 4, Table 2); the yields were 0.12, 0.10 and 0.73 mmol of **1**, **2** and **3**, respectively. On the other hand, the yield of **1** was the highest (0.47 mmol) under 30 atm of CO pressure where the yield of **3** was minor (0.13 mmol) (entry 5). Further

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

Entry	T (°C)	CO (atm)	Propane (atm)	$Co(OAc)_2$ (mmol)	Time (h)	Products(mmol)[b]			Yield (%)[c]
						1	**2**	**3**	
1	60	40	6	0.1	15	0.33	0.08	0.05	9.0
2	70	40	6	0.1	15	0.44	0.13	0.12	12.6
3	80	40	6	0.1	15	0.43	0.13	0.35	12.3
4	70	1	6	0.1	15	0.12	0.10	0.73	4.9
5	70	30	6	0.1	15	0.47	0.13	0.13	13.2
6	70	30	1	0.1	15	0.34	0.10	0.24	58.0
7	70	30	2	0.1	15	0.42	0.12	0.23	36.0
8	70	30	7	0.1	15	0.54	0.16	0.15	13.2
9	70	30	7	0.01	15	0.13	0.04	0.18	3.2
10	70	30	7	0.3	15	1.01	0.32	0.21	25.1
11	70	30	7	0.1	30	0.65	0.17	0.25	15.5

[a] TFA (5 mL) used. [b] GC yield. [c] Based on propane.

increase of CO pressure beyond 30 atm resulted in low yields of all the products (entry 2). Under high pressure of CO, the oxidation of the Co(II) species to higher valent would probably be difficult[2c] so that the hydrogen abstraction which is supposed to be the initial step in this reaction from hydrocarbons, RH to yield $R^{\cdot}$ radical, may become slow.

Under 1 atm of propane (entry 6), the reaction gave high yields of **1**, **2** and **3** (total yield 89.5% and yield of acids 58%, based on propane), however, it is highest in quantities under 7 atm (entry 8). High pressure of propane also facilitates the formation of the C–C bond rather than that of the C–O bond in this reaction. On the other hand, the turnover number (TON) of the catalyst is the highest, 8.5 (entry 8) when 0.1 mmol of catalyst and 7 atm of propane were used. The use of amounts of catalyst smaller and greater than 0.1 mmol exhibits lower TON (entries 9 and 10) although the larger amount (0.3 mmol) of catalyst gave the highest yield (entry 10).

The yields of **1** and **2** increased until 30 h (0.65 and 0.17 mmol, respectively) (entry 11). In the prolonged reaction time beyond 30 h the yields of **1** and **2** decreased, possibly due to the thermal decomposition of the products, whereas the yield of **3** increased constantly.

After optimizing the conditions, we attempted the same reaction of various saturated hydrocarbons as shown in Table 3. Methane and ethane reacted slightly, giving only the carboxylated products in low yields (0.02 and 0.03 mmol, respectively) (entries 1 and 2). In the case of ethane, 0.2 mmol of acetic acid was also formed. Ester product (0.25 mmol) was dominantly formed in the reaction of cyclopentane rather than acid product (0.21 mmol) (entry 4). A remarkably high yield (39%) was obtained in the case of cyclohexane where the acid product was the major one (entry 5). On the other hand, cycloheptane hardly reacted with CO in this reaction, giving 0.05 mmol of acid and 0.11 mmol of ester (entry 6).

The activation parameters (Ea, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and $\Delta G^{\ddagger}{}_{343}$) for the formation of *iso*- and *n*-butyric acids and *iso*-propyl trifluoroacetate in the reaction of propane (5 atm) with CO (30 atm) in the presence of $Co(OAc)_2$ (0.1 mmol), $K_2S_2O_8$ (5 mmol) and TFA (5 mL) for 30 min within the temperature range of 65 and 80°C have been determined by the Arrhenius and the Eyring plots and the results are listed in Table 4. Although the cause of the different values of $\Delta S^{\ddagger}$ for the formation of **1** and **2**, the values of Ea and $\Delta S^{\ddagger}$ (for the formation of **2** and **3**) are comparable with the activation energy for the formation of methyl radical in the Li/MgO catalyzed oxidative coupling of methane[7] and the entropy change for the activation of neopentane by $CpRh(CO)_2$.[8]

Table 3
Carboxylation reaction of various hydrocarbons[a]

Entry	Substrate	Product (mmol)[b]		Yield (%)[c]
		acid	ester	acid
1	CH_4[d]	0.02	--	0.1
2	C_2H_6[e]	0.03	--[f]	0.4
3	$CH_3CH_2CH_3$[g]	*iso*-0.34 *n*-0.10	0.24	58.0
4	*c*-C_5H_{10}	0.21	0.25	21.0
5	*c*-C_6H_{12}	0.39	0.21	39.0
6	*c*-C_7H_{14}	0.05	0.11	5.0

[a] Conditions: Catalyst (0.1 mmol), *c*-hydrocarbon (1 mmol), $K_2S_2O_8$ (10 mmol), CO (30 atm) and TFA (5 mL), 70 °C, 30 h. [b] Determined by GC. [c] Based on hydrocarbon. [d] CH_4 (30 atm), [e] C_2H_6 (10 atm). [f] Acetic acid (0.20 mmol) was formed. [g] propane (1 atm, 0.76 mmol), 15 h.

Table 4
Activation parameters of the formation of each product

Product	*Ea* kcal/mol	A mol m^3/s	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$ cal/mol K	$\Delta G^{\ddagger}_{343}$ kcal/mol
1	29.6	1.44×10^{13}	29.0	-0.52	29.2
2	25.2	1.32×10^{10}	24.6	-14.43	29.6
3	27.6	7.20×10^{10}	27.0	-11.05	30.8

1, *iso*-Butyric acid; **2**, *n*-Butyric acid; **3**, *iso*-Propyl trifluoroacetate.

Although the mechanistic scenario of this reaction remains unclear, the higher valent cobalt species formed in the reaction mixture would be expected to be an active species in this reaction. $Co(OAc)_2$ is readily oxidized to the higher valent species such as Co_{ox}[9] or superoxocobalt(III) ($Co^{(III)}$-O-O$^{\cdot}$). The homolytic thermal decomposition of the O–O bond of the cobalt(III) species can give the $Co^{(III)}$-O$^{\cdot}$ radical[10] which would attack the alkane molecule, RH, abstracting the hydrogen atom to form the alkyl radical ($R^{\cdot}$) which is quickly trapped by CO to yield an acyl radical ($RCO^{\cdot}$). The latter species is assumed to be converted to the carboxylic acid (RCOOH) via the formation of mixed anhydride with TFA.[11] The additional oxygen atom of the carboxylic acid may come from the TFA through the formation of an intermediate.

In summary, the carboxylation reaction of saturated hydrocarbons especially propane gave high yields of the corresponding carboxylic acids as the dominating products. The esterified products also formed in this reaction as by products in various yields depending on the reaction conditions. The activation parameters for the formation of **1**, **2**, and **3** have been determined and are quite consistent with the reported values.[7,8]

Acknowledgements

This work was supported in part by the Grants-in-Aid for Scientific Research on Priority Area No. 283 'Innovative Synthetic Reactions' and Scientific Research (A) No. 09355031 from the Ministry of Education, Science, Sports and Culture of Japan.

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6. Representative procedure: 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) and 5 mL of TFA was introduced. Then the autoclave was closed and flushed with carbon monoxide three times and finally pressurized with carbon monoxide (30 atm). Then the autoclave was heated with stirring at a fixed temperature for the desired length of time. After cooling and venting the residual gases, the autoclave was opened and the mixture was analyzed directly by GLC-8A (Unisole 10T+H_3PO_4). The ester products of methane, ethane and propane were determined by NMR spectra.
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