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Production of Methane by Catalytic Decarboxylation of Methyl Formate as a Liquid Surrogate

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ABSTRACT: Methane is a widely utilized molecule, primarily sourced from fossil fuels and it finds numerous applications in the energy sector. More sustainable sources of methane include the conversion of organic wastes or gaseous CO₂. An alternative would be to use a sustainable C₁ intermediate able to form methane. To this end, this work demonstrates the utilization of methyl formate as a liquid surrogate for methane, and its selective decomposition by catalytic decarboxylation. This reaction exhibited excellent yields, exceeding 90%, and the method can be expanded to produce several alkanes from alkyl formates.

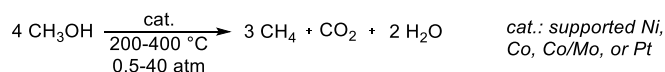
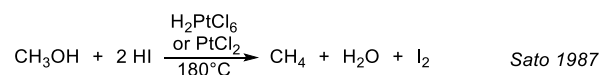
INTRODUCTION

Natural gas is mostly composed of methane and accounts for 25 % of the primary energy consumed in the world, totaling 3.94 billion m³ in 2022.¹⁻² The current extraction of natural gas is primarily sourced from fossil fuels. However, efforts to transition towards more sustainable productions have led to the development of alternative methods. Some companies aim to reduce their carbon footprint by producing and using local, low-carbon energy. Biogas facilities employ anaerobic digestion to produce methane,³⁻⁴ and methane can also be produced by the chemical hydrogenation of CO₂ to methane (the Sabatier reaction).⁵⁻¹⁰ The former method relies on methanogens, capable of digesting organic wastes in anaerobic conditions.¹¹⁻¹⁵ This process produces methane in a mixture with CO₂, which requires further purification. Conversely, the direct CO₂ hydrogenation to methane, often proceeds at elevated temperature and pressure (200-400°C, 5-15 bar).

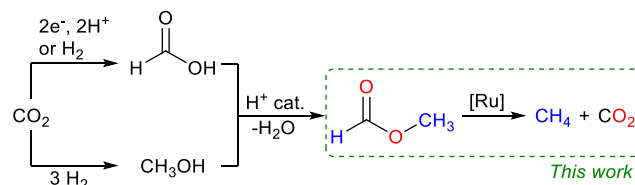
To achieve methane production from sustainable sources and milder conditions, one idea involves conducting the reaction in stages through an intermediary C₁ molecule capable of yielding methane. Methanol emerges as a viable candidate for this intermediary because it is the C₁ compound with the closest oxidation state to methane. It can be produced from CO₂ hydrogenation,¹⁶⁻¹⁸ a process implemented in Iceland with the “George Olah CO₂ to renewable methanol plant” demonstrates the maturity of the process.¹⁹ Nevertheless, the reduction of the C–O bond of methanol is challenging and requires most of the time heterogeneous metal catalysts working under harsh conditions (typical conditions use 300-400°C, under 0.5-40 bar of H₂).²⁰⁻²⁶ In the homogenous phase, Sato imagined in 1987 a reaction to form methane from methanol in the presence of two equivalents of a strong acid (HI) and a platinum catalyst (Scheme 1, top).²⁷ Low amount of methane was also observed by Foster when using an iridium catalyst and an iodide promoter in the carbonylation of methanol.²⁸ Although the reaction conditions are harsh, Sato’s strategy remains, to our knowledge, one of the few homogeneous paths, together with hydrosilylation,²⁹⁻³¹ to produce methane starting from methanol. In a broader context, many strategies are used for directly reducing

alcohols to alkanes in organic synthesis, including the Barton-Mac Combie reaction, the use of hydrosilanes,³²⁻³⁵ the oxidation-Wolff Kischner sequence,³⁶⁻³⁸ the dehydration-hydrogenation sequence,³⁹⁻⁴¹ and others.⁴²⁻⁴⁴ However, these methods do not apply to methanol and require relatively toxic reagents and/or generate waste that adds to processing challenges. As an alternative to these shortcomings, we propose to reduce methanol with formic acid (FA) via the intermediate formation of methyl formate, FA being itself obtainable from CO₂ electroreduction⁴⁵⁻⁴⁷ or hydrogenation (Scheme 1, bottom).⁴⁸⁻⁵¹

Literature examples for the reduction of methanol to methane



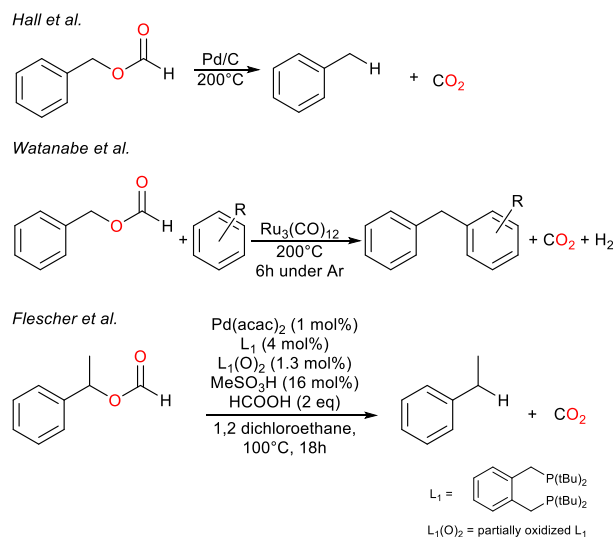
Proposed strategy: utilization of methyl formate



Scheme 1. top: Representative examples for the reduction of methanol to methane. Bottom: strategy for the use of methyl formate as a liquid surrogate for methane

Methyl formate is readily obtained by esterification of FA with methanol. It has been recently proposed as a hydrogen energy carrier thanks to ruthenium catalysts.⁵² When using it as a liquid surrogate for methane, the main challenge relies in designing an efficient decarboxylation of this alkyl formate. Research into the decomposition of methyl formate has mainly focused on its decarbonylation via isomerization to acetic acid.⁵³ In some conditions, methane could be seen, like in Pruet’s

work on the isomerization of methyl formate with an iridium catalyst and methyl iodide as a promoter in the presence of water, which led to the inhibition of the formation of acetic acid in favor of methane.⁵⁴ Only few examples have been reported in the literature for the decarboxylation of organic formates and they mostly concern activated benzyl formates (Scheme 2). In 1970, Hall used palladium on carbon at 200 °C to convert benzyl formate to toluene with a yield of 97%.⁵⁵ Watanabe used benzyl formate as a benzylating reagent for arenes through decarboxylation using $[\text{Ru}_3(\text{CO})_{12}]$ at 200 °C.⁵⁶ However, the reactive benzyl cation or radical formed under these conditions can activate the C–H bond in benzene, making recombination with the hydride to form toluene challenging with $[\text{Ru}_3(\text{CO})_{12}]$ alone. In 2015, Fleischer demonstrated a single-step esterification and reductive decarboxylation from benzylic alcohols and formic acid using a palladium complex and an acid additive.⁵⁷ To our knowledge, the only example of activation of the C–O bond of an alkyl formate other than benzyl formate has been reported by Jenner, who showed that under CO, $[\text{Ru}_3(\text{CO})_{12}]$, and methyl iodide as an additive, methyl formate isomerizes to acetic acid at 200 °C.^{58–60} Interestingly, minor quantities of methane were also formed as side-products. Herein, we report on the selective decarboxylation of methyl formate into methane, its scale up, and the extension of the catalytic methodology to other alkyl formates.



Scheme 2: State of the art in the decarboxylation of benzyl formates

RESULTS AND DISCUSSION

Starting with the system proposed by Jenner, we wished to quantify the amount of methane produced in the absence of CO, upon decomposition of methyl formate with $[\text{Ru}_3(\text{CO})_{12}]$: When methyl formate is heated at 160 °C in the presence of 3 mol% of $[\text{Ru}_3(\text{CO})_{12}]$ and 20 mol% of LiI in THF, we observed after 24 h a conversion of 55 % of the starting methyl formate, and some methane could be observed in ^1H NMR. However, we also observed the formation of 14 % of methanol and 13 % of methyl iodide, from the decarbonylation and nucleophilic substitution of methylformate respectively. No other liquid product was observed in ^1H NMR, leading us to conclude that the remainder consisted of methane and CO_2 , both identifiable in the GC chromatogram (Figure 1).

The decarboxylation reaction thus led to the formation of methane in 28 % yield. In order to improve the efficiency and the selectivity, we considered a plausible mechanism with intertwined catalytic cycles that involve: (i) facilitating the cleavage of the C–O bond of methyl formate by nucleophilic substitution, using lithium iodide, to form methyl iodide and lithium formate, (ii) decarboxylating the formate on the catalyst to form a metal hydride intermediate and (iii), transferring this hydride equivalent to methyl iodide, yielding methane (Scheme 3).⁶¹

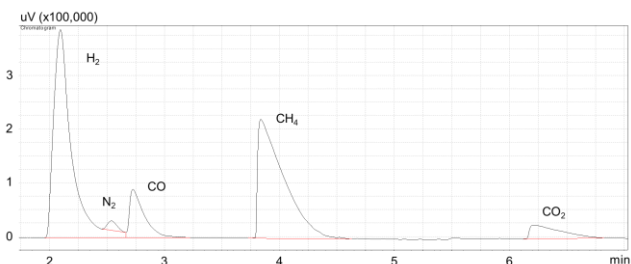
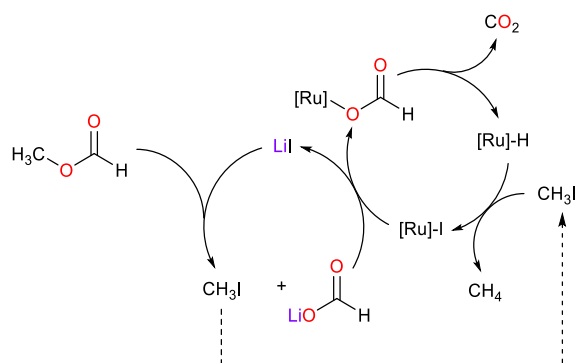


Figure 1: Analysis of the head fraction of the gaseous phase of the experiment with $\text{Ru}_3(\text{CO})_{12}$ as a catalyst (3 mol%) and lithium iodide as an additive (20 mol%) after 3 days of reaction at 160 °C



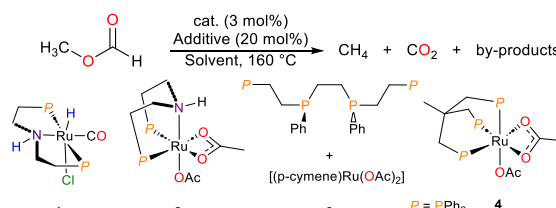
Scheme 3. Proposed mechanism for the formation of methane from methyl formate

First, a screening of catalysts was performed, using four ruthenium complexes known for their ability to form hydride species and/or perform decarboxylation reactions.^{62–63} The decarboxylation of methyl formate was first tested with 3 mol% of $[(\text{MACHO})\text{RuH}(\text{CO})\text{Cl}]$ **1**, efficient in the transfer hydrogenation of esters.⁶² After 3 days at 160 °C in the presence of 20 mol% of LiI, we observed 23 % conversion, but only methyl iodide and methanol were observed by ^1H NMR in 15 and 8 % yield respectively (Table 1, Entry 1). The acetate complex $[(\text{MACHO})\text{Ru}(\text{OAc})_2]$ **2** led to lower conversion and only side-products were detected. (Table 1, Entry 2.). The combination of *rac*-P4 and $[(p\text{-cymene})\text{Ru}(\text{OAc})_2]$ **3** was also tested, as it was described by Gonsalvi *et al.* to be efficient in the decarboxylation of formic acid to H_2 and CO_2 .⁶³ The conversion is significant (95 %) after 3 days, and only traces of methyl iodide and 7 % methanol are observed (Table 1, Entry 3). Finally, $[(\text{triphos})\text{Ru}(\text{OAc})_2]$ **4**, also used in the disproportionation of formic acid,^{64–65} was found to be the most efficient catalyst and full conversion was observed after 24 h, resulting in the selective formation of methane in 95 % yield: only traces of methanol and methyl iodide were observed (Table 1, Entry 4). Lowering the temperature to 100 °C was however detrimental to the catalytic activity, which drastically decreased, and only 8% of methyl formate was converted into methanol and methyl iodide:

no methane was observed in ^1H NMR (Table 1, Entry 5). Blank experiments (Table 1, Entries 5 and 6) confirmed that both LiI and the ruthenium complex are required to obtain methane. Furthermore, LiI alone is able to form iodomethane, which supports our mechanistic hypothesis where iodomethane is a key intermediate of the reaction.

The influence of the solvent was then tested: replacing THF with an apolar solvent, benzene- d_6 , led to a very low (12 %) conversion and mostly methyl iodide was observed (Table 1, Entry 8.). In acetonitrile, the reaction did not form methane or methyl iodide, and only methanol as well as unidentified peaks were detected (Table 1, Entry 9), which may arise from the decomposition of acetonitrile.⁶⁶ In DMF- d_7 , methane was formed in 73 % yield, albeit together with 24 % of methanol after three days of reaction (Table 1, Entry 10).

Table 1 Optimization of reaction conditions



Entry	Cat.	Addit.	Solvent	Conv. (%) ^[a]	CH ₃ I (%) ^[a]	CH ₃ OH (%) ^[a]	CH ₄ (%) ^[b]
1	1	LiI	THF- d_8	23	15	8	-
2	2	LiI	THF- d_8	14	< 5	< 5	-
3	3	LiI	THF- d_8	95	< 5	7	86
4 ^[c]	4	LiI	THF- d_8	100	< 5	< 5	95
5	4	-	THF- d_8	-	-	-	-
6	-	LiI	THF- d_8	14	11	< 5	-
7 ^[c,d]	4	LiI	THF- d_8	8	5	< 5	-
8	4	LiI	C ₆ D ₆	12	8	< 5	-
9	4	LiI	CD ₃ CN	80	- ^[e]	9	- ^[e]
10	4	LiI	DMF- d_7	97	-	24	73
11	4	LiI / LiBF ₄	THF- d_8	19	19	-	-
12	4	LiBr	THF- d_8	69	< 5 ^[f]	< 5	64
13	4	NaI	THF- d_8	< 5	-	-	-
14	4	KI	THF- d_8	< 5	-	-	-
15	4	Ph ₄ PI	THF- d_8	< 5	-	-	-

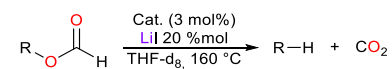
Reaction conditions : 0.14 mmol MeOCHO, 3 mol% catalyst, additive 20 mol%, 0.6 mL solvent, 3 days, 160 °C, [a] Determined by ^1H RMN of crude mixture, mesitylene was used as internal standard, [b] computed by difference between conversion and yield of liquid products (ESI for more details), [c] reaction time of 24 h, [d] 100 °C, [e] degradation of acetonitrile, [f] CH₃Br

Other additives were also tested, starting with LiBF₄ which, according to Han,⁶⁷ facilitates the cleavage of the C–O bond in aryl methyl ethers. In that case however, the catalytic activity was totally lost even though methyl iodide was still formed (Table 1, Entry 11). Switching lithium iodide to use larger cations such as potassium, PPh₄⁺, or sodium was also deleterious to the catalytic activity, and no conversion was observed (Table 1,

Entries 13, 14 and 15.). Replacing LiI with LiBr allowed the formation of methane in 64 % yield, with only traces of MeBr and MeOH (Table 1, Entry 12). Such modifications did not improve the catalytic activity further, and we continued to use 3 mol% of **4**, together with 20 mol% of LiI, in THF, at 160 °C, for the rest of the study. Incidentally, on this optimized system, when methyl formate and LiI are replaced by a 1:1 mixture of lithium formate and methyl iodide, we observed, after 24 h at 160 °C, a conversion of 78 % and an intense peak of methane in ^1H NMR, confirming our previous mechanistic hypotheses.

We then tested this system to other alkyl formates to assess its versatility. The reactions were performed under optimized conditions, monitoring the reaction by ^1H NMR until the maximum conversion was reached (Table 2). While full conversion for methyl formate was obtained in 24 hours (Table 2, Entry 1), ethyl formate was decomposed much more slowly (91 % conversion in 7 days), mainly producing ethane together with traces of the decarbonylation product (ethanol) and the elimination product, ethylene (Table 2, Entry 2). No reaction was observed with butyl formate. When benzyl formate was used, full conversion was observed in less than 48 hours, but the selectivity dropped, and only 48 % toluene was obtained (Table 2, Entry 3). Side-products include 32 % of benzyl alcohol and 8 % of benzaldehyde. These compounds may have been formed through decarbonylation of the formate, leading to benzyl alcohol. The latter can be further dehydrogenated to benzaldehyde.⁶⁸ To enhance selectivity, we employed the more sterically hindered catalytic system **3** expected to exhibit reduced C–H bond insertion in benzyl formate, thus minimizing decarbonylation. As anticipated, this led to improved selectivity, with 84% toluene observed after 48 hours of heating (Table 2, Entry 4).

Table 2 Catalytic decarboxylation of selected alkyl formates



Entry	Substrate (R)	Cat.	Reaction time ^[b]	Conv. (%) ^[c]	Observed products
1	CH ₃	4	24 h	100	CH ₄ < 5 % CH ₃ OH < 5 % CH ₃ I
2	CH ₃ CH ₂	4	7 days	91	C ₂ H ₆ major 7% CH ₃ CH ₂ OH C ₂ H ₄ traces
3	Ph-CH ₂	4	48 h	100	48% PHCH ₃ 32% PhCH ₂ OH 8 % PhCHO 12% PhCH ₂ I
4	Ph-CH ₂	3	48 h	98	84% PHCH ₃ < 5 % PhCH ₂ OH 8 % PhCHO

[a] Reaction conditions: 0.14 mmol alkyl formate, 3 mol% catalyst, LiI 20 mol%, 0.6 mL THF- d_8 , 160 °C. [b] Reaction time for maximum conversion. [c] Determined by ^1H RMN of the crude mixture, mesitylene was used as internal standard

Finally, to showcase the applicability of the reaction on a larger scale, the decarboxylation of methyl formate was carried out in a 50 mL Parr autoclave (Scheme 4). For this experiment, the concentration of methyl formate and the volume of the reaction were increased respectively from 0.24 M and 0.6 mL at NMR scale to 0.7 M and 8 mL. After 3 days of reaction, we were

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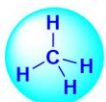
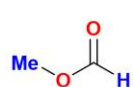
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ToC Artwork:

Liquid surrogate of
Methane



[Ru] catalyst

