

# FORMATE AND ACETATE STABILITY UNDER REPOSITORY RELEVANT CONDITIONS: WHAT CAN WE LEARN FROM THE LITERATURE?

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## Introduction

<sup>14</sup>C is an important dose-determining radionuclide in L/ILW repositories due to its potential release in the form of dissolved or gaseous species facilitating its migration from the disposal site into the biosphere.

<sup>14</sup>C-formate and <sup>14</sup>C-acetate are the main <sup>14</sup>C bearing organic compounds released during anoxic corrosion of irradiated steel under repository relevant conditions. The fate of these <sup>14</sup>C-bearing organic compounds after their release from the irradiated steel waste, however, is still largely unknown.

After closure, partially saturated conditions might exist for up to 100'000 years due to gas production in the near field. Hence reactions both in gas and aqueous phase are possible.

Thermodynamically, formate and acetate are unstable and decompose to CO<sub>2</sub> or CH<sub>4</sub>. At moderate temperatures, however, these redox reactions are extremely slow and formate and acetate can be metastable for very long times.

In the literature, few data exist on the abiotic decomposition of formate and acetate at temperatures below 100° C because decomposition is expected to occur mainly by microbiological activity. Extensive research has been carried out under high temperature and pressure conditions in the gas phase (catalysis) and under hydrothermal conditions found in e.g., sedimentary basins and oil-field brines. This contribution presents a summary of insights obtained from these high temperature and pressure data and their relevance for the stability of formate and acetate under L/ILW repository conditions.

## Approach

- Comparison of rates of different formate and acetate decomposition reactions described in the literature
- Effect of temperature described with the Arrhenius law
- Extrapolation of the decomposition rate to temperature relevant to L/ILW repository

Decomposition rate, r

$$r = \frac{d[C]}{dt} = -k \cdot [C]^n$$

C = compound concentration (M)

n = reaction rate: n = 1: 1th order    n = 2: 2nd order

k = rate constant (s<sup>-1</sup> for n = 1;    s<sup>-2</sup> for n = 2)

$$[C] = [C]_0 \cdot e^{-kt} \quad (n = 1)$$

$$\frac{1}{[C]} = k \cdot t + \frac{1}{[C]_0} \quad (n = 2)$$

Effect of temperature (Arrhenius law)

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T}$$

A = pre-exponential factor (s<sup>-1</sup> for n = 1; s<sup>-2</sup> for n = 2)

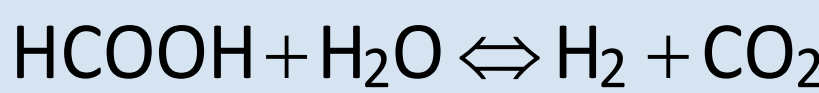
E<sub>a</sub> = activation energy (J mol<sup>-1</sup>)

## Formate decomposition

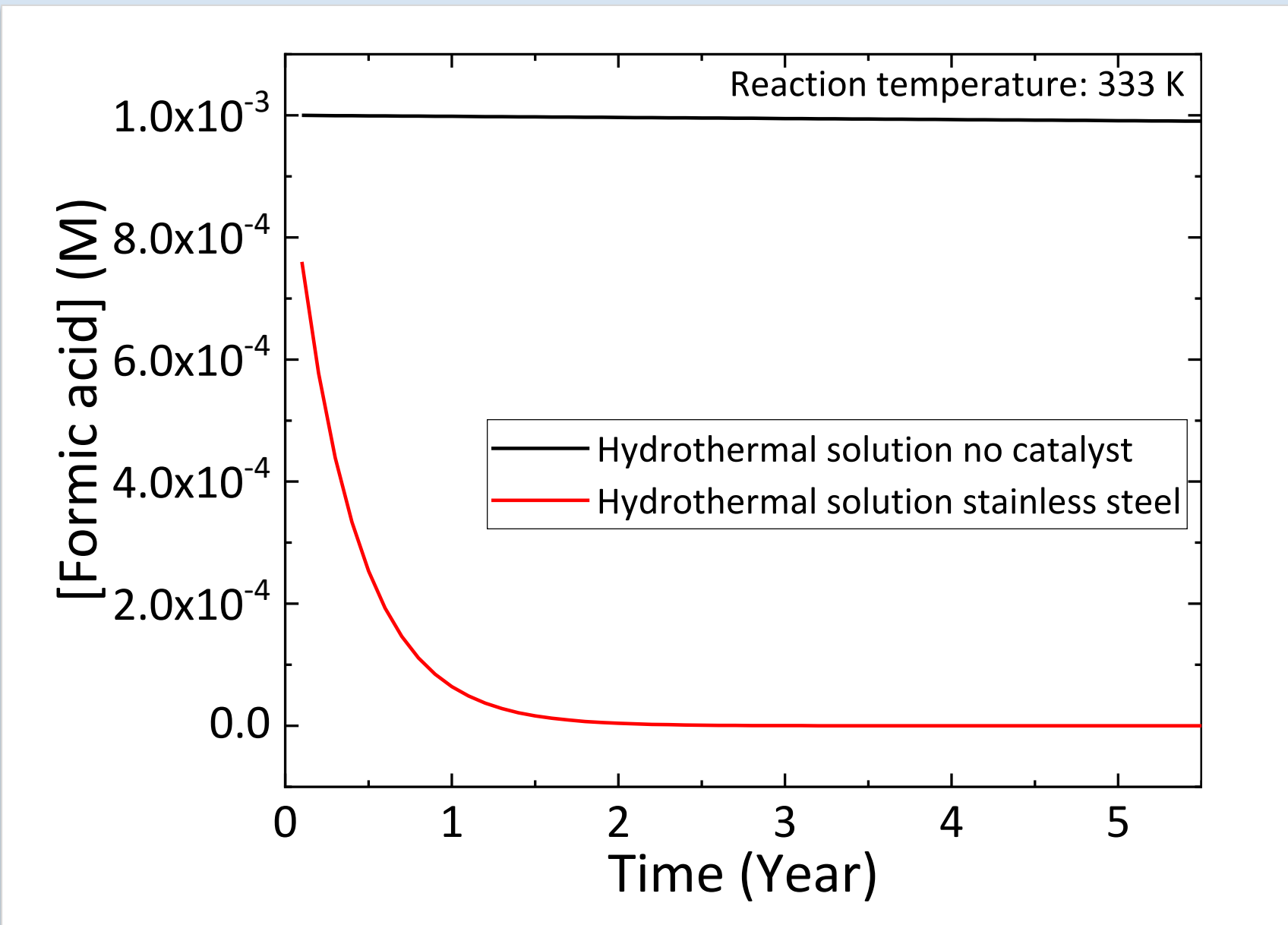
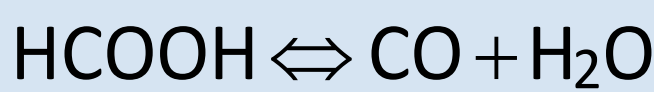
	Chemical conditions	Catalytic surface	Reaction	Reaction order	lnA	E <sub>a</sub> kJ mol <sup>-1</sup>	Temp. Range	Ref.
Formic acid	Gas phase in absence of H <sub>2</sub> O	No catalyst Fe(100)	Dehydration	2	~31.8 (M <sup>-1</sup> s <sup>-1</sup> )	251 - 293	700K-800K	1) 2)
			Decarboxylation		~31.3 (M <sup>-1</sup> s <sup>-1</sup> )	272 - 301		3)
			Dehydration Decarboxylation	1	~31.8 (s <sup>-1</sup> )	130.0	298K-800K	4) 5)
	Gas phase in presence of H <sub>2</sub> O vapour	No catalyst	Dehydration	1	~26.7 (s <sup>-1</sup> )	209.0	Ab initio calc.	6)
			Decarboxylation		~27.9 (s <sup>-1</sup> )	189.5		
	Hydrothermal solutions	No catalyst	Decarboxylation	1	10.2 (s <sup>-1</sup> )	93.6	448K-533K	7)
Formate	Hydrothermal solutions	Steel	Decarboxylation	1	13.0 (s <sup>-1</sup> )	80.7	448K-533K	7)
		Ti-metal	Decarboxylation	1	8.9 (s <sup>-1</sup> )	70.9	448K-533K	7)
		No catalyst	Decarboxylation	1	15.9 (s <sup>-1</sup> )	120.9	448K-533K	7)

Decomposition reactions:

Decarboxylation:



Dehydration:

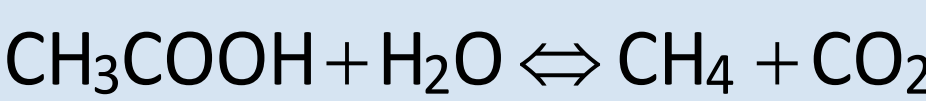


## Acetate decomposition

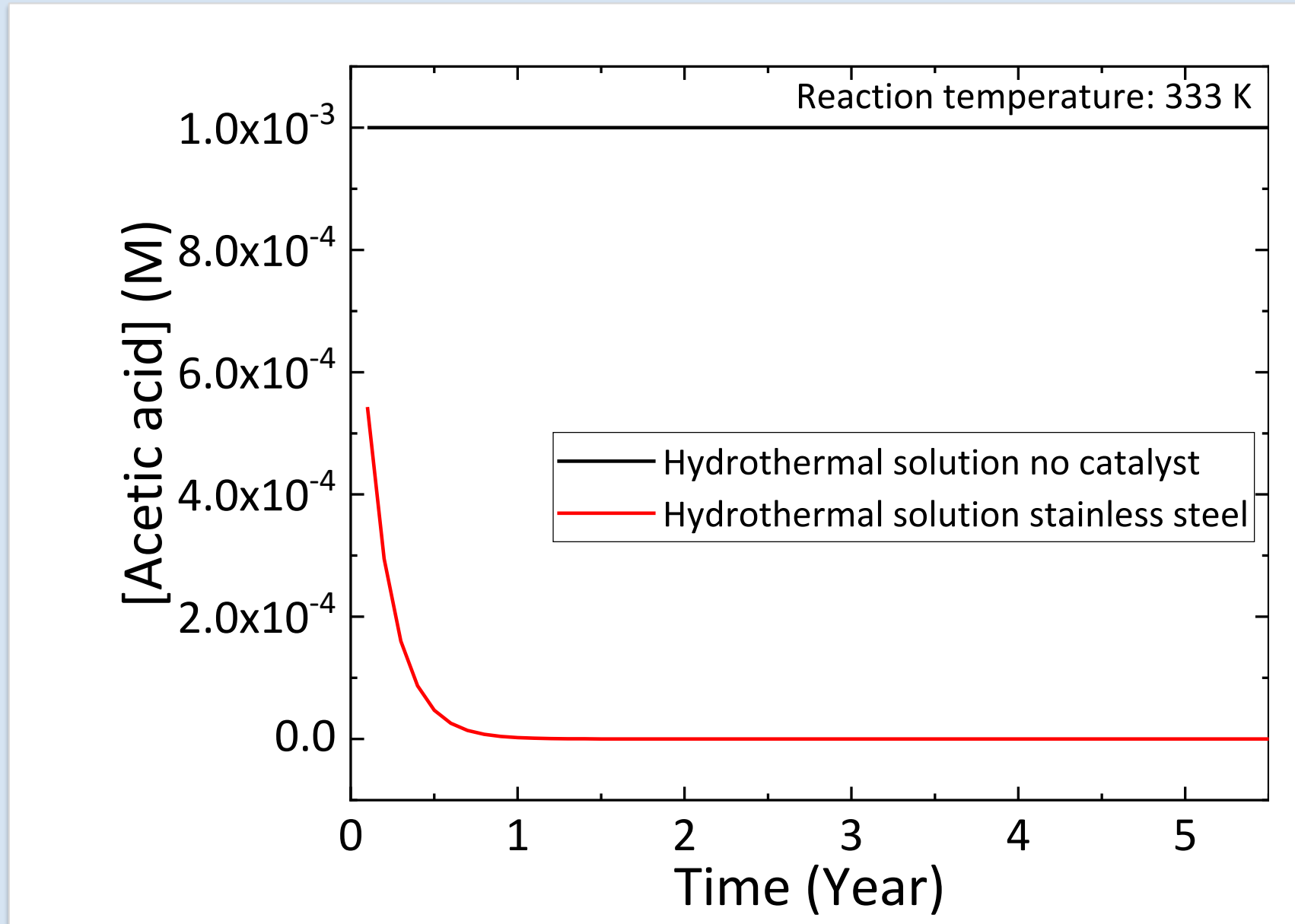
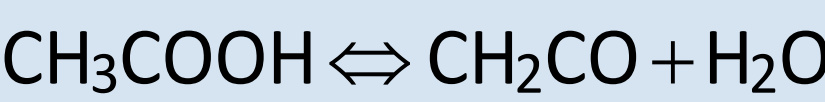
	Chemical conditions	Catalytic surface	Reaction	Reaction order	lnA	E <sub>a</sub> kJ mol <sup>-1</sup>	Temp. range	Ref.
Acetic acid	Gas phase in absence of H <sub>2</sub> O	No catalyst	Dehydration	2	21.9 (s <sup>-1</sup> )	164	430K-1190K	8) 9)
			Decarboxylation	1	31.3 (s <sup>-1</sup> )	292.0		
			Ketonisation below 673 K	1				
	Gas phase in presence of H <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	Ketonisation	1				
		Magnetite	Ketonisation	1				
		Magnetite	Reduction to acetaldehyde	1				
Acetate	Hydrothermal conditions	No catalyst	Decarboxylation	1	21.7 (s <sup>-1</sup> ) ~13.5 (s <sup>-1</sup> )	205 130	608K-628K 403K-653K	10) 11)
		Stainless steel	Decarboxylation	1	13.8 (s <sup>-1</sup> )	34	473K-573K	12)
		Stainless steel	Decarboxylation	1	40.5 (s <sup>-1</sup> )	290	608K-628K	10)

Decomposition reactions:

Decarboxylation:



Dehydration:

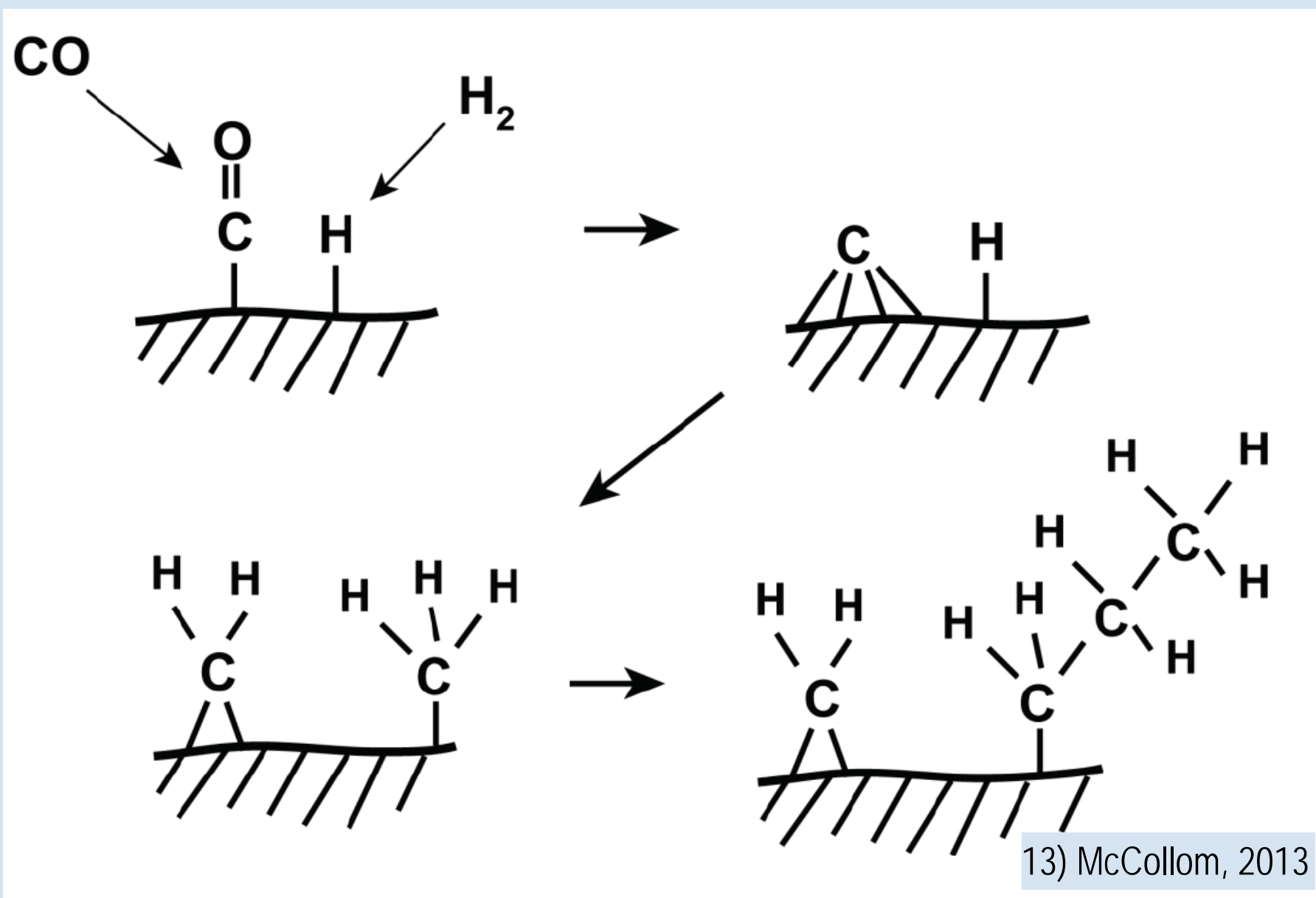


## Fischer-Tropsch synthesis

Fischer-Tropsch synthesis reactions: Transformation of CO and CO<sub>2</sub> in organic compounds via reduction and polymerisation reactions on the surface of catalysts.

Only possible under very specific conditions:

- 1) In aqueous solution at high levels of dissolved H<sub>2</sub> and T and P approaching the critical point (647 K or 374° C and 22.06 MPa)
- 2) In hydrothermal systems below 573 K in the presence of high levels of dissolved H<sub>2</sub> and NiFe alloy, FeCr-oxide or magnetite
- 3) At temperatures below 573 K in H<sub>2</sub>-rich, H<sub>2</sub>O saturated vapour phase



## Summary

Formic acid and acetic acid can decompose both in the gas phase and in the aqueous phase. Activation energies for the decomposition of both organic compounds are the lowest under aqueous conditions in the presence of stainless steel as a catalyst. Under these conditions, predictions based on decomposition rate constants extrapolated from high temperature experiments, suggest that both organic compounds should be decomposed completely within a short period of time.

In the gas phase of a partially saturated near field and in the presence of high H<sub>2</sub> partial pressures and an appropriate catalyst (e.g., Fe-bearing solids), the decomposition products, CO<sub>2</sub> and CO, might further react via a Fischer-Tropsch-type mechanism to produce longer chain hydrocarbons.

## References

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