HYDROTHERMAL REACTIONS OF LACTIC ACID CATALYSED BY GROUP VIII METAL COMPLEXES

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Summary

At 220–250°C, in the presence of $[PtH(PEt_3)_3]^+$ in aqueous solution, α-hydroxy-propanoic acid (lactic acid) is converted into propanoic, propenoic, β-hydroxypropanoic, pyruvic and acetic acids. The reactions catalysed by $[PtH(PEt_3)_3]^+$ appear to be double bond hydration and hydrogenation, alcohol dehydration, transfer hydrogenation, decarbonylation and the water-gas shift reaction. Propenoic acid under similar conditions gives similar products. Attempts to catalyse the dehydrocarboxylation of lactic acid using $PdCl_2$, $[PtCl_2(PPh_3)_2]$, $[IrH(CO)(PPh_3)_3]$ and $[Ni(CO)_2(PPh_3)_2]$ were partially successful, although competing disproportionation gave a wide range of products.

Introduction

The decarboxylation of unactivated carboxylic acids is of prime importance in biomass liquefaction schemes. In general, decarboxylation reactions have been carried out oxidatively (e.g. the Kolbe reaction), but these are not catalytic processes. Although loss of carbon dioxide is thermodynamically favourable for both activated and unactivated carboxylic acids, the high transition state energies involved present considerable practical difficulties. Several catalytic decarboxylation cycles encompassing organometallic intermediates can be envisaged. However, the few catalytic examples of decarboxylation reactions that have been reported [1] have all been heterogeneous, e.g. over Ni/Al_2O_3 and Pd/SiO_2 catalysts, although a related homogeneously catalysed reaction is the decarboxylation of acid anhydrides by nickel catalysts [2].

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TABLE 1

HYDROTHERMAL REACTIONS OF LACTIC AND PROPENOIC ACIDS CATALYSED BY $[PtH(PEt_3)_3]^+$

Substrate	Temperature (°C)	Time (h)	pH	Products (mol, %) [a]						
				Propanoic acid (19.3)	β-Hydroxy-propanoic acid (14.5)	Pyruvic acid (8.2)	Propenoic acid (21.4)	Acetone (24.1)	Acetic acid (16.1)	Lactic acid (13.2)
Lactic acid	230	2	2 [b,c]	43	24	1	3.4	1	3	15
	220	3	2 [h]	31	23	0.1	0.6	1	2.1	4.7
	250	0.25	2 [c]	50.5	24	–	1.1	–	6.3	2.2
	220	2	7 [d]	19	–	13.0	–	1	0.1	33
	180	2	7	2.6	–	6.1	0.05	–	–	62
	220 [e]	2	2	36	10	–	1.0	–	–	13
Propenoic acid	180	2 [f]	2	17	14	14	1.6	–	3.1	–
	180	2 [g]	7	8.5	3.3	13.3	1.3	–	2.1	2.2

[a] Data taken from HPLC results, based on initial lactic acid, ±10%; retention times (RT) in min. [b] Small amounts (< 5%) of an unidentified product (RT 8.2 mins) were obtained. [c] Small amounts (< 5%) of an unidentified product (RT 22 mins) were obtained. [d] pH at end of reaction 4.5. [e] Catalyst was Pt/Al_2O_3 (5%). [f] Two unidentified products (RT 2.4 mins, 40%) and (RT 6.5 mins, 20%) were also present. [g] CH_3CHO (RT 17.06 mins), trace.

The decarboxylation of formic acid, however, is a facile process and has recently been reported [3] by using the catalysts [Pt(PR$_3$)$_3$] where R = Et or i-Pr. Our own observations [4–7] of catalysis in aqueous solution using similar catalysts prompted us to investigate the activity of [Pt(PEt$_3$)$_3$] with the unactivated acid, α-hydroxypropanoic acid (lactic acid).

We report the results of these studies which reveal the catalysis in water of a number of disproportionation reactions.

Results and discussion

1. Disproportionation of lactic acid in sealed ampoule experiments

Heating aqueous solutions of lactic acid in water (pH 2) containing [Pt(PEt$_3$)$_3$] which is present as the protonated product [8], [PtH(PEt$_3$)$_3$]$^+$, at 220–250°C for 2 h leads to the conversion of lactic acid to the products shown in Table 1. The expected product of decarboxylation, ethanol, was not observed. The principal product is propanoic acid in yields of 2–50%. This is accompanied by other products, including β-hydroxypropanoic, acetic, propenoic and pyruvic acids. Similar products are obtained at pH 7, although in lower yields, only ca. 40–60% conversion of lactic acid being observed after 2 h at 180–220°C. The reaction was homogeneous in the lower temperature range (< 200°C) but insoluble brown material was observed at higher temperatures. This may have resulted from catalyst decomposition or decomposition of pyruvic acid (charring occurs when aqueous pyruvic acid is heated to 220°C in the absence of catalyst). However, we have carried out the reaction using Pt/Al$_2$O$_3$ as a heterogeneous catalyst and similar results are obtained (Table 1). In the absence of a catalyst, lactic acid is recovered unchanged under these conditions.

The formation of propenoic acid suggests that dehydration of lactic acid is occurring. This proposed dehydration appears to be unprecedented in organometallic catalysis. On thermodynamic grounds, the dehydration of alcohols is unlikely, and indeed, the reverse reaction occurs for propenoic acid (Table 1). Most of the propenoic acid arising from lactic acid dehydration is removed by subsequent hydrogenation and rehydration reactions. Certain reactions are likely to be pH dependent, for example, hydration and dehydration. Changes in the position of the hydration/dehydration equilibrium with pH would account for the observed lower conversions at pH 7 than at pH 2.

The appearance of the principal product, propanoic acid, can be explained in terms of a catalytic hydrogen transfer step from lactic acid to propenoic acid giving propanoic and pyruvic acids. Pyruvic acid may also be formed by direct dehydrogenation of lactic acid and, indeed, this step is implied in the transfer hydrogenation mechanism [9].

The formation of β-hydroxypropanoic acid can be attributed to rehydration of propenoic acid, giving lactic acid or β-hydroxypropanoic acid (See Scheme 1). In the hydration of cyanoethene catalysed [10] by [PtH(PEt$_3$)$_3$]$^+$, the main product is 2-hydroxypropionitrile, in which the hydroxo group has added to the carbon atom of the double bond which is β to the electron-withdrawing cyano group. This product is expected to be thermodynamically favoured and our observations suggest that β-hydroxypropanoic acid is similarly favoured over lactic acid as the major hydration product of propenoic acid under the conditions employed here (Table 1). Care must be taken in interpreting these results, however, since it is possible that the small
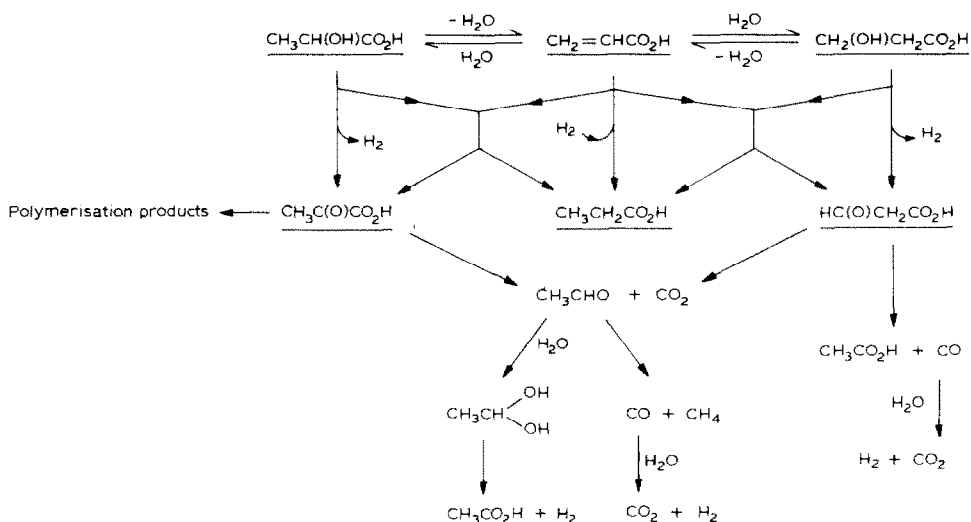
SCHEME 1. Proposed reactions of lactic acid in aqueous solution. All reactions are catalysed by $[PtH(PEt_3)_3]^+$ with the possible exception of pyruvic acid decarboxylation and polymerisation; detected products are underlined.

amounts of lactic acid produced from propenoic acid may reflect a greater ease of dehydrogenation to pyruvic acid (in the transfer hydrogenation reaction) compared with dehydrogenation of β-hydroxypropanoic acid.

Possible sources of the minor product, acetic acid are: (a) the decarbonylation of malonic semialdehyde, the β-keto-acid formed from transfer hydrogenation by the β-hydroxypropanoic acid; and (b) the dehydrogenation of acetaldehyde hydrate (see Scheme 1).

The yields of propanoic acid are generally higher than expected on the basis of Scheme 1, even after allowance for the decomposition of pyruvic acid under these conditions to give charred species and polymeric materials. To explain these high yields of propanoic acid it is necessary to propose that hydrogenation of propenoic acid by a hydrogen source other than α or β-hydroxypropanoic acid occurs. This hydrogen source is likely to be molecular hydrogen *, formed from CO and water (i.e. the water gas shift reaction, which is known [12] to be catalysed by $[PtH(PEt_3)_3]^+$). The carbon monoxide could be produced from catalytic decarbonylation of acetaldehyde (in turn, formed from the decarboxylation of pyruvic acid or more likely, malonic semialdehyde). Alternatively hydrogen could be derived from the dehydrogenation of acetaldehyde hydrate (see Scheme 1).

The probable mechanism of the dehydration reaction (reverse of the hydration step) is shown in Scheme 2. This involves coordination by an alcoholic function followed by γ-hydrogen transfer [14] to give a metal–carbon σ-bond. Loss of OH$^-$ then occurs, either by protonation or by direct transfer to the metal. The former is more likely since the reverse reaction probably occurs by nucleophilic attack by

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* Related complexes of platinum are known [13] to be active for hydrogenation of alkenes under molecular hydrogen.
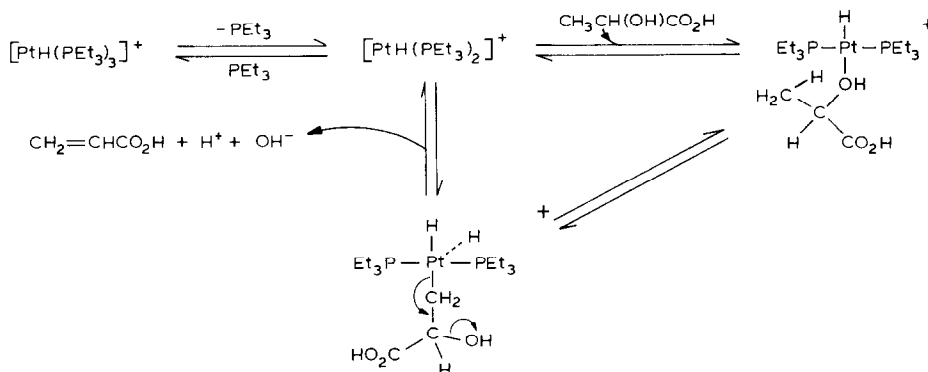
SCHEME 2. Proposed mechanism of dehydration of lactic acid.

water or OH^- on the coordinated alkene (cf. the Wacker process [15] and the hydration of alkynes [16]).

2. Reverse Reppe, dehydrocarboxylation reaction

The metal catalysed reaction for the conversion of alkenes to saturated carboxylic acids [17], hydrocarboxylation (eq. 1), can be reversed provided that the volatile products and water are continuously swept from the solution [18].

$$RCH=CH_2 + CO + H_2O \rightarrow RCH_2CH_2COOH \qquad (1)$$

$$CH_3CH(OH)COOH \rightarrow CH_3CHO + CO + H_2O \qquad (2)$$
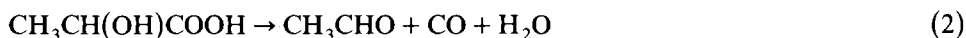
When lactic acid is used (reaction 2), the expected products are acetaldehyde, CO and water. We have, therefore, carried out the reaction of lactic acid with a number of different catalysts, the volatile products being driven off in a Dean–Stark apparatus.

The products shown in Table 2, in particular the large amount of acetaldehyde formed, suggest that some success in driving the reverse Reppe reaction is achieved with $PdCl_2/PPh_3$, $[PdCl_2(PPh_3)_2]$ and $[IrH(CO)(PPh_3)_3]$. However, since most of the products can also be rationalised in terms of the reactions of Scheme 1, the exact mechanism of their formation is uncertain.

It is evident that although the desired direct decarboxylation of lactic acid by organometallic complexes could not be achieved, various other interesting catalytic reactions take place in aqueous solution.

Experimental

$[Pt(PEt_3)_3]$ was prepared by a standard method [19]. The complexes $[PdCl_2]$, $[PdCl_2(PPh_3)_2]$, $[IrH(CO)(PPh_3)_3]$ and $[Ni(CO)_2(PPh_3)_2]$ were obtained from Strem Chemical Company. d,l-Lactic acid (technical grade 80%, from Aldrich Chemical Company) was used without further purification.

Lactic acid disproportionation products were analysed by high pressure liquid chromatography (HPLC) using a Bio-rad HX87 'organic acid' type ion exclusion column operated at 10°C. Eluant was 0.0125 N H_2SO_4, flow rate 0.6 cm^3/min^{-1}

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TABLE 2

ATTEMPTED REVERSE REPPE REACTIONS OF LACTIC ACID AT pH 2

Catalyst	Temperature (°C)	Time (h)	Products (mol, %) [a]					Gaseous phase
			Propanoic acid	Propenoic acid	Lactic acid	Acetaldehyde	Methanol	
PdCl$_2$/PPh$_3$/NaCl	220	3	48	2.0	6.7	21.5	3.3	CH$_3$CHO
cis-[PdCl$_2$(PPh$_3$)$_2$]/ NaCl	220	1	35	–	5.4	10	4.9	CH$_3$CHO
cis-[PtCl$_2$(PPh$_3$)$_2$]/ [b] NaCl+[PtH(PPh$_3$)$_3$]$^+$	150–180	1	28	2.1	2.0	24	13	CH$_3$CHO, H$_2$, CO
[IrH(CO)(PPh$_3$)$_3$]/ NaCl	160	4	36	–	10	10	12.3	(CH$_3$)$_2$CO, CO, CO$_2$, C$_2$H$_4$, C$_3$H$_8$
[Ni(CO)$_2$(PPh$_3$)$_2$] [c]	160	4	4.5	3.3	5	2	19	

[a] In Dean–Stark trap and residue flask; based on initial lactic acid. Data based on HPLC results. [b] Additional product; formic acid 2.0%. [c] Additional product: acetone 3.3%.

and the products were detected by an Altex refractive index detector. Gaseous samples were analysed by gas chromatography (GC) using an 8 ft. stainless steel column packed with Poropak R. The carrier gas was helium at 20 cm^3 min^{-1} and the column temperature was programmed from 30° to 180° at 20°C min^{-1}.

GC/mass spectral results were obtained using a Finnegan 4000 and INCOS data system and Porapak QS 6 ft, 2 mm ID column. The carrier gas was helium at 25 cm^3 min^{-1} and the column temperature programmed from 140 to 180° at 10°C min^{-1}.

Catalytic reactions

(a) Lactic acid disproportionation. Solutions containing lactic acid (0.5 g, 5.6 × 10^{-3} mol) and [PtH(PEt$_3$)$_3$]OH (0.02 g, 3.5 × 10^{-5} mol) in water (1 cm^3) were sealed into glass Carius tubes under vacuum. They were heated to the required temperature (Table 1) in a thermostatted oil bath. After 2 h they were removed, cooled to ca. −30°C and opened for analysis. The solutions were always homogeneous at the start of the reaction, but at the higher temperatures (> 220°C) some precipitation of a brown-grey material occurred. From the yellow supernatant solutions, the remaining platinum complex could be recovered by precipitation with NaBPh$_4$ (0.048 g, 1.4 × 10^{-4} mol) to give [PtH(PEt$_3$)$_3$](BPh$_4$); ν(Pt–H) 2100–2200 cm^{-1}, ^{1}H NMR showed δ(Pt–H) 15 ppm, doublet of triplets, (yield 8.2 mg, 27%).

For reactions at pH 7, the pH was adjusted with KOH (0.1 M) before heating.

Reactions involving propenoic acid (1.05 g, 0.0145 mol) and [PtH(PEt$_3$)$_3$]OH (0.02 g 3.5 × 10^{-5} mol) were carried out as described for lactic acid.

Pt/Al$_2$O$_3$ (5% PtAl$_2$O$_3$, 10 mg) was added to a solution of lactic acid (0.5 g, 5.6 × 10^{-3} mol) in water (1 cm^3) and the suspension heated in a sealed tube as described above.

(b) Dehydrocarboxylation reactions. The catalyst (0.57 mmol) was suspended in water (30 cm^3) containing lactic acid (18 g, 0.2 mol) and NaCl (0.4 g, 6.9 × 10^{-3} mol) and the mixture heated to the temperature shown in Table 2 for 2 h in a Dean–Stark apparatus. The gaseous effluent, the residue and the material collected in the Dean–Stark trap were all analysed by GC and HPLC techniques.

Acknowledgements

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