Aerobic oxidation of diols to acetic acid in water

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ABSTRACT

The aerobic oxidation of 1,2-propandiol and 2,3-butanediol in water in the absence and presence of a heterogeneous PtCu-based catalysts has been carried obtaining acetic acid as the most abundant organic compound in solution. Catalytic reactions carried out with reaction intermediates in the absence of catalysts clearly showed that only the diol oxidation to the corresponding hydroxy ketone is PtCu-catalyzed, while the further oxidation is radical based.

Introduction

Acetic acid (AA) is an important platform used for the synthesis of vinyl acetate, acetic acid anhydride and esters which find application as solvents for inks, paints and coatings [1]. In addition, AA is food additive and preservative with anti-microbial activity [1]. Hence biomass-derived diols such as 1,2-propandiol (1,2-PD) (*i.e.* obtained by hydrogenolysis of glycerol [2–5]) or 2,3-butandiol (2,3-BD) (*i.e.* microbial production by the aid of efficient microbial strains [6,7]) in combination with a robust heterogenous catalysts might be an interesting alternative to the less sustainable methanol carbonylation under homogeneous reaction conditions [8]. Since the discovery of the vicinal diol cleavage by the usage of stoichiometric amounts of toxic oxidants like lead tetra carboxylates and periodates, many heterogeneous metal nanoparticle (NP)-based catalysts have been successfully employed in the aerobic *vic*inal diol cleavage, leading either to carbonyl compounds or carboxylic acids [9]. Herein is presented the oxidative cleavage of 1,2-PD and 2,3-BD in water under aerobic conditions in the absence and presence of the heterogenous catalyst **1**, which gave notable results in the aerobic oxidation of ethanol to AA [10].

Experimental

Materials has been synthesized as previously reported [10]. 1,2-PD, 2,3-BD, 3-OH-2-BO, 2,3-BD and H_2O-d_2 were purchased form Aldrich and used as received.

Analytical methods

^{1}H NMR spectra were acquired at room temperature by using a Bruker Avance 400 MHz spectrometer and H_2O-d_2 as solvent.

HPLC analyses were carried out with a Shimadzu apparatus equipped with an Aminex HPX-87H column (300 mm × 7.8 mm, BIO RAD) and a RID 10A detector. Analyses were conducted by applying a flow rate of the eluent (i.e. sulfuric acid, 0.005 M) of 0.4 mLmin^{-1} and a column temperature of either 35 or 65 °C, according to the substrate used. The quantification of all organic compounds involved in the catalytic oxidation reactions were based on calibration curves determined for each compound.

GC analyses of the autoclave's head space was carried out by means of a Shimadzu 2010 apparatus, equipped with a TCD-17 detector and a Carboxen (Supelco) 1010 PLOT fused silica capillary column (30 m × 0.32 mm). He was used as carrier gas.

The FT-IR spectrum was acquired at room temperature as KBr pellet using a Perkin Elmer BX FT-IR spectrometer.

The powder X ray diffraction (PXRD) spectrum was acquired at room temperature with a PANalytical X'PERT PRO powder diffractometer, using Cu Kα radiation (λ = 1.5418 Å) and a Si zero background wafer as sample holder.

Catalytic reactions

A teflonated autoclave (320 mL) was successively charged with substrate (13.7 mmol), water (50 mL) and **1**. The autoclave was then sealed, pressurized with air, electrically-heated at 140 °C and mechanical stirred. After the latter temperature had been reached, the air pressure was adjusted to 20 bar and stirring continued for the desired reaction time. The autoclave was then cooled by means of an ice water bath to 10 °C and a fraction of the head space gas was withdrawn and analyzed by GC-TCD, whereas the remaining gas was vented off, the
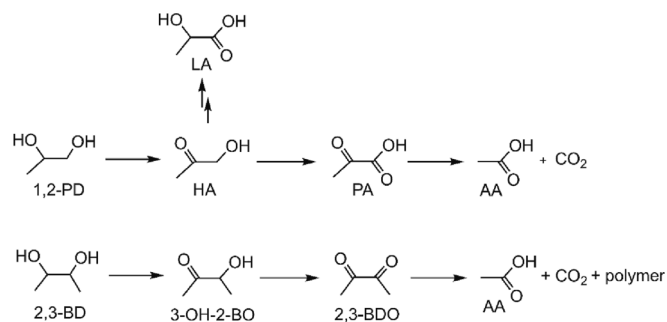
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Scheme 1. Sequence of reaction products obtained in the aerobic oxidation of 1,2-PD and 2,3-BD to AA.

Table 1
Aerobic oxidation of 1,2-PD under neutral reaction condition.[a]

Entry	Conv. (%)	Sel. (HA)(%)	Sel. (PA)(%)	Sel. (LA)(%)	Sel. (AA)(%)
1[b]	<2	n.d.	n.d.	n.d.	n.d.
2	83.7	11.6	3.3	7.0	78.0
3[c]	<1	n.d.	n.d.	n.d.	n.d.
4[d]	89.8	6.2	0.1	7.9	85.9
5[d,e]	64.7	8.3	1.3	12.7	77.7
6[b,f]	97.7	–	–	4.9	90.1

[a] Catalytic condition: **1** (0.97 μmol Pt), 1,2-PD (13.7 mmol), water (50.0 mL), p (air) = 20 bar at 140 °C, t (17 h), T (140 °C). [b] Without catalyst. [c] Under N_2 atmosphere (20 bar). [d] t = 24 h. [e] 1,2-PD (27.4 mmol). [f] HA (13.7 mmol); FA (5.0%) detected.

suspension centrifuged and the clear solution analyzed by HPLC and ^{1}H NMR spectroscopy using an Evans tube charged with H_2O-d_2.

The substrate conversion given in mmol and as percentage was defined as follows: mmol (subst. initial) - mmol (subst. recovered); 100 × [mmol (subst. initial) - mmol (subst. recovered)] / mmol (subst. initial).

The products' selectivity given in percentage was defined as follows: 100 × [mmol (product) / Σmmol (products)].

Results and discussion

1,2-PD and 2,3-BD were converted to AA under aerobic oxidation conditions (water solution of the alcohols, 0.27 M; T = 140 °C; p(air) = 20 bar, t = 17 h) in the absence and presence of **1**, consists in diamine-stabilized PtCu NPs with a Pd to Cu molar ratio of 1, supported onto a high surface area carbon (Ketjenblack) [10]. In Scheme 1 are shown the sequences of reaction products intercepted by HPLC and ^{1}H NMR spectroscopy during the aerobic oxidation of the above diols to AA.

A blank reaction of 1,2-PD gave an almost negligible conversion (<2%, Table 1, entry 1).

In contrast, the same reaction conducted in the presence of **1**, significantly increased the 1,2-PD conversion yielding hydroxy acetone (HA), pyruvic acid (PA), lactic acid (LA) acetic acid (AA) and CO_2 (Scheme 1), which have been intercepted by HPLC (Fig. S1) and ^{1}H NMR spectroscopy (Fig. S2). The presence of CO_2 in head space of the autoclave was proved by GC-TCD (Fig. S3) and thus confirmed that AA has been generated by the decarboxylation of PA [11]. Under the latter experimental conditions an AA selectivity of 78.0% was obtained (Table 1, entry 2). LA has been formed as side reaction, which comprises the conversion of HA to pyruvaldehyde, which successively undergoes an intramolecular Canizzaro reaction [11]. An identical catalytic reaction conducted in the presence of a nitrogen atmosphere converted only trace amounts of 1,2-PD (Table 1, entry 3). The latter experimental result is in accordance with the experimental fact that hydrogen, stemming from dehydrogenation of 1,2-PD to HA, was not intercepted in the

Table 2
Aerobic oxidation of 2,3-BD under neutral reaction condition.[a]

Entry	Substrate	Conv. (%)	Sel. (3-OH-2-BO)(%)	Sel. (2,3-BDO)(%)	Sel. (AA) (%)
1[b]	2,3-BD	12.0	38.7	24.2	37.1
2	2,3-BD	93.6	19.6	13.9	66.5
3[c]	2,3-BD	<1	–	–	–
4[b,d]	3-OH-2-BO	99.5	–	21.2	76.4
5[b,c]	3-OH-2-BO	<1	n.d.	n.d.	n.d.
6[b,e]	2,3-BDO	93.0	–	–	91.4

[a] Catalytic condition: **1** (1.94 μmol Pt), 2,3-BD (13.7 mmol), water (50.0 mL), p (air) (20 bar), t (17 h), T (140 °C). [b] Without catalyst. [c] Under N_2-atmosphere (20 bar). [d] Formation of 2,3-BD (2.4%). [e] Acetone (8.6%).

head space of the autoclave and hence the catalytic reaction did not proceed under hydrogen-acceptorless reaction condition [12,13], instead oxygen is needed as final oxidant giving water as reaction product.

On prolonging the reaction time to 24 h the AA selectivity increased to 85.9% on the expense of HA selectivity, while the LA selectivity remained comparable to that obtained after an identical catalytic reaction lasting 17 h (Table 1, entry 4 vs 2). On the other hand, a higher concentration of 1,2-PD (0.548 M) led to a significant drop of the AA selectivity to 77.7%, which is mainly due to a more pronounced LA formation (i.e.12.7% vs 7.9%), whereas the HA selectivity was comparable (8.3% vs 6.2%) (Table 1, entry 5 vs 4). This latter result, is indicating that the HA conversion to AA is fast and that a high HA concentration fosters the LA synthesis. Importantly, LA has not been found to convert into PA under the chosen experimental conditions [11]. In order to prove the reactivity of HA under aerobic oxidation reaction conditions, we conducted a blank reaction with the latter substrate and found an almost HA conversion into AA with a selectivity of 90.1% (Table 1, entry 6), giving LA and formic acid (FA) as side products. Hence HA was transformed into AA without the need of an additional catalyst, underscoring the high reactivity of carbonyl compounds under aerobic oxidation reaction conditions [14].

A blank reaction conducted with a water solution of 2,3-BD (0.27 M), characterized by a *meso/rac*-molar ratio of 9:1, showed under identical catalytic conditions (140 °C, p(air) = 20 bar and reaction time of 17 h) a conversion of 12.0% into 3-hydroxy-2-butanone (3-OH-2-BO), 2,3-butanedione (2,3-BDO), AA and CO_2 (Scheme 1, Table 2, entry 1).

The same catalytic reaction lasting 24 h and conducted in the presence of **1** showed a 2,3-BD conversion of 93.6% along with an increase of the AA selectivity to 66.5% (Table 2, entry 2). The reaction products obtained have been analyzed by HPLC (Fig. S3) and ^{1}H NMR spectroscopy (Fig. S4). The notable difference in 2,3-BD conversion observed in the absence and presence of **1**, under otherwise identical catalytic conditions confirmed that the 2,3-BD to 3-OH-2-BO conversion is the rate determining step in the aerobic conversion of 2,3-BD into AA. The conversion of 2,3-BD carried out in the absence of oxygen has shown to be negligible (Table 2, entry 3).

The conversion of 3-OH-2-BO (0.27 M) into AA proceeded almost quantitatively even in the absence of **1** giving AA in 76.4% selectivity (Table 2, entry 4), while the same reaction in the absence of air gave a negligible 3-OH-2-BO conversion (<1%, Table 2, entry 5), confirming the importance of oxygen during the dehydrogenation of 3-OH-2-BO (i.e. hydrogen acceptor). In this context, it is important to mention that also 2,3-BD (2.4%) was obtained during the aerobic oxidation of 3-OH-2-BO, underscoring the experimental fact, that 3-OH-2-BO functioned to some extend as hydrogen acceptor. The aerobic oxidation of 2,3-BDO conducted in the absence of **1**, gave AA in 91.4% selectivity (Table 2, entry 6) along with acetone (8.6%) (Fig. S5), CO_2 (Fig. S6) and a solid polymeric material. The powder - X ray diffraction spectrum of the latter solid showed a narrow Bragg reflex centered at 18.02° (2Θ) (Fig. S7),

Table 3

1-catalyzed aerobic oxidation of 1,2-PD, 2,3-BD and ethanol in water.[a]

Substrate	Conv. (mmol/%)	Sel. AA (%)	AA (mmol)	Percentage of substrate converted into AA (%)
Ethanol [10]	97.5	98.0	10.0	73.0
1,2-PD	83.7	78.0	4.4	32.1
2,3-BD[b]	93.6	66.5	4.0	14.6

[a] Catalytic condition: **1** (Pt, 0.97 μmol), substrate (13.7 mmol), water (50.0 mL), T (140 °C), t (17 h), p(air) (20 bar).

[b] **1** (Pt, 1.94 μmol); AA yield given in percentage referred to the amount of C_2-units of 2,3-BD.

which is in agreement with the formation of a crystalline polymeric material. The formation of acetone and of polymeric material is a strong hint for radical-based reaction mechanism, which is operative during the aerobic C-C bond cleavage of the dione in water [15]. The polymeric material might be formed by the polymerization of ketene, generated by the decomposition of an acetyl peroxo radical [16], which is known to be a reactive monomer for polymerization reactions [17,18]. An FT-IR spectrum of the latter brown polymer (Fig. S8) confirmed the presence of a polyketone structure.

A comparison of the AA yield gained by the **1**-catalyzed aerobic oxidation reaction of 1,2-PD, 2,3-BD and ethanol [10] as substrate, using identical experimental conditions as reported in Table 3, clearly showed that the aerobic oxidation of ethanol and 2,3-BD gave the highest and lowest AA yield, respectively, (Table 3, 73.0% *vs* 14.6%), which is mostly due to the formation of polymeric material and CO_2 in case of 2,3-BD.

Conclusions

In the present study the usage of 1,2-PD and 2,3-BD, which are important bio mas-deriving diols, as substrate for the catalytic transformation into AA upon applying aerobic oxidation reaction conditions showed that: (*i*) The diol conversion to the first intermediate (*i.e.* hydroxy ketone) is a metal nanoparticle-catalyzed reaction, whereas (*ii*) the latter compound converts to AA and CO_2 also in the absence of catalyst, confirming that hydroxy ketones are reactive intermediates and follow a radical-based mechanism to yield AA. The precursor for AA is either pyruvic acid (1,2-PD) or the dione 2,3-BDO, which undergo a decarboxylation and a dione cleavage, respectively to obtain the C2 unit of AA. Unfortunately, the dione cleavage is not a clean process generating not only CO_2, but also acetone and a polymeric material, which originates from the polymerization of "in situ" formed ketene. Hence a comparison of the AA yield obtained by the aerobic oxidation of ethanol and both above mentioned diols by applying the same heterogeneous catalyst [10] and the same experimental conditions showed the following order: EtOH (73.0%) > 1,2-PD (32.1%) ≫ 2,3-BD (14.6%) (the yield of AA in case of 2,3-BD is referred to two C2 units per molecule of 2,3-BD).

Data availability

Data will be made available on request.

CRediT authorship contribution statement

Werner Oberhauser: Investigation, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data (HPLC traces and ^{1}H NMR spectra of the catalytic solutions, head space analysis by GC-TCD, PXRD and FT-IR spectra of the isolated solid material after aerobic 2,3-BDO oxidation) to this article can be found online at https://doi.org/10.1016/j.rechem.2023.100897.

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