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ORIGINAL RESEARCH

Stability of gamma-valerolactone under neutral, acidic, and basic conditions

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Abstract Dry gamma-valerolactone (GVL) is stable for several weeks at 150 °C and its thermal decomposition only proceeds in the presence of appropriate catalysts. Since GVL does not react with water up to 60 °C for several weeks, it could be used as a green solvent at mild conditions. At higher temperatures, GVL reacts with water to form 4-hydroxyvaleric acid (4-HVA) and reaches the equilibrium in a few days at 100 °C. Aqueous solutions of acids (HCl and H_2SO_4) catalyze the ring opening of GVL even at room temperature, which leads to the establishment of an equilibrium between GVL, water, and 4-HVA. Although the 4-HVA concentration would be below 4 mol% in the presence of acids, it could be higher than the concentration of a reagent or a catalyst precursor, not to mention a catalytically active species. The latter could be especially worrisome as 4-HVA could be an excellent bi- or even a tridentate ligand for transition metals. Aqueous solution of bases (NaOH and NH_4OH) also catalyzes the reversible ring opening of GVL. While in the case of NaOH, the product is the sodium salt of 4-hydroxyvalerate, the reversible reaction of GVL, with NH_4OH results in the formation of 4-hydroxyvaleric amide. The reversible ring opening of (*S*)-GVL in the presence of HCl or NaOH has no effect on the stability of the chiral center.

Keywords Gamma-valerolactone · Water · 4-hydroxy-valeric acid · Sulfuric acid · Hydrochloric acid · Ammonium hydroxide · Solvents · Equilibrium · Stability

Introduction

Solvents are important to provide one or more liquid phases for chemical reactions and processes [1]. While some solvents are available from nature [2], even in large quantities such as water, most of the solvents are man-made from fossil resources [3]. Traditionally, solvents were developed and/or selected primarily to achieve chemical and/or physical objectives and the impacts of their widespread use on the environment and/or health were not seriously considered until the emergence of green chemistry [4]. One of the key principles of green chemistry is the elimination of solvents in chemical processes or the replacement of hazardous solvents with environmentally benign solvents. Furthermore, the development of solvent-free processes has been suggested as the best prevention, especially when either one of the substrates or the products is a liquid and can be used as the solvent. However, if a solvent is required, the selection of a green solvent with no or limited impact on health and the environment should be preferred [5].

Gamma-valerolactone (GVL) is a cyclic ester containing a methyl group at the fifth position of a dihydrofuran-2(3H)-one

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Dedicated to Professor George A. Olah on the occasion of his 90th birthday.

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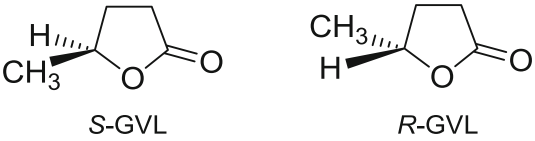
ring. Although the (*S*) and (*R*) enantiomers of GVL have been known [6], most investigations have used its racemic form. We have

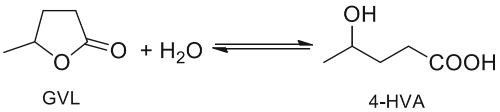


realized 10 years ago that GVL exhibits the most important characteristics of an ideal sustainable liquid [7–10] and could be used as a green solvent [2] or a feedstock for the production of both carbon-based consumer products [8, 11] and energy [7–10, 12]. GVL is renewable, occurs naturally, and used by the food industry frequently as a food additive. It has low melting (−31 °C), high boiling (207 °C), and flash (96 °C) points, a pleasant smell for easy recognition of leaks and spills, low toxicity, and high solubility in water to assist biodegradation. In addition, its vapor pressure is low, 0.65 kPa at 25 °C, and increases five times to 3.5 kPa at 80 °C [10].

The thermal stability of GVL is remarkably high and only 1% decomposed when a mixture of GVL and N_2 (1:10 mol/mol) was heated at 600 °C in a continuous reactor with a residence time of approximately 400 ms at 0.17 MPa [13]. By increasing the temperature to 800 °C, 98% of GVL decomposed, initially to 4-pentenoic acid, 1-butene, and CO_2 (Scheme 1), followed by the formation of typical products of high temperature radical decomposition. Isomerization of 4-pentenoic acid and 1-butene as well as other fragmentation reactions was also observed [13].

Isotope labeling experiments with $H_2{}^{18}O$ have established that GVL does not react with water under neutral conditions at room temperature for 3 months or at 60 °C for 28 days [10]. Since GVL does not form an azeotrope with water [10, 14], the latter can be readily removed by distillation resulting in a less energy demanding process for the production of GVL than that of absolute ethanol [15]. Furthermore, GVL does not form a measurable amount of peroxides in a glass flask under air in weeks, making it a safe material for large scale use [16].

It was also shown by using $H_2{}^{18}O$, that GVL undergoes a reversible reaction with water in the presence of hydrochloric acid to form 4-hydroxyvaleric acid (4-HVA) [10] (Scheme 2) and the equilibrium lies far to the left at room temperature. The presence of small amount of 4-HVA was also observed during the conversion of $^{13}C_6$-labeled fructose to $^{13}C_5$-GVL in the presence of sulfuric acid in GVL as solvent [17].



Scheme 2 Reversible reaction of GVL with water

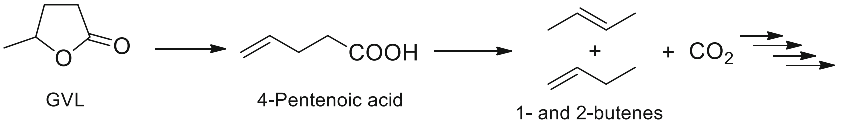
It should be noted that either at very high temperatures [13] or in the presence of acids at lower temperatures, the isomerization of 4-pentenoic acid and 1-butene as well as other fragmentation reactions proceed readily [18–20].

Olah and Ku reported that GVL can be completely protonated with HSO_3F-SbF_5 in liquid SO_2 to form two stable isomeric species in 75:25 ratio at −80 °C (Scheme 3), indicating a hindered rotation along the protonated C=O bond [21].

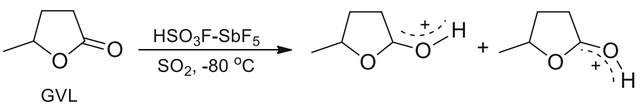
The potassium salt of 4-hydroxyvalerate was prepared by the ring-opening reaction of GVL with aqueous KOH (Scheme 4), which was then used to prepare the silver salt of 4-hydroxyvalerate [22]. The formation of the sodium salt of 4-hydroxyvalerate by the reaction of GVL with NaOH was confirmed by NMR [10]. While the reaction of GVL with aqueous NH_4OH resulted in 4-hydroxyvaleric amide, other aliphatic primary and secondary amines were used to prepare 4-hydroxy-N-alkyl or -dialkyl valeric amides [23]. Similarly, GVL has reacted with tetraalkylammonium hydroxydes to form tetraalkylammonium 4- hydroxyvalerates [24].

It was shown that GVL is one of the best solvents for acid catalyzed conversion of carbohydrates to levulinic and formic acids [25]. The selective hydrogenation of levulinic acid to 4-HVA was performed in GVL–water mixture by the use of homogeneous Ru catalysts [26]. GVL was shown to be an excellent solvent for heterogeneous Pd-catalyzed Hiyama [27], Heck [28], Sonogashira [29], and Catellani [30] reactions. Synthesis of GVL in GVL from paper wastes [12] as well as from corn stover and rice husk [31] was demonstrated by a one pot system containing sulfuric acid and the Shvo catalyst. The heterogeneous catalytic C–H arylation of 1,2,3-triazoles in GVL was used in the synthesis of pharmaceuticals [32]. The application of GVL as the reaction medium for Pd-catalyzed asymmetric hydroformylation and aminocarbonylation has also been reported [33, 34].

Since GVL has become a popular green solvent [35, 36], we report our studies on the stability of GVL in neutral, basic, and acidic conditions, which should help chemist and chemical engineers to decide how to use GVL as a green solvent.



Scheme 1 Decomposition of GVL at higher temperatures



Scheme 3 Protonation of GVL by HSO_3-SbF_5 in liquid SO_2 at -80 °C

Materials and methods

Gamma-valerolactone, 37.0% HCl, 98% H_2SO_4, 25% NH_4OH, biphenyl, dimethyl sulfone ($DMSO_2$), and 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS-Na) were obtained from Sigma-Aldrich Ltd., Hong Kong. Thirty-seven percent DCl was purchased from Armar Chemicals. d_6-Dimethyl sulfoxide (DMSO) and deuterium oxide (D_2O) were obtained from Cambridge Isotope Laboratories, Inc. Levulinic acid, (*S*)-[(RuCl(SEGPHOS))$_2$(μ-Cl)$_3$][NH$_2$Me$_2$], and (*S*)-GVL were purchased from Sigma-Aldrich Ltd., Budapest, Hungary.

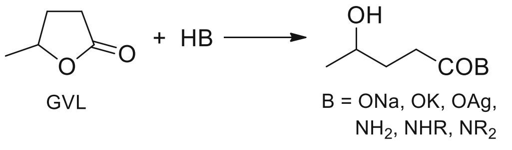
Dry GVL was prepared by stirring 100 mL GVL with about 5 g P_2O_5 for 3 days at room temperature followed by vacuum distillation at 65 °C and 1.5 Hgmm.

The NMR experiments were carried out using Bruker AV III 300 or 400 or 600 MHz instruments. For quantitative ^{1}H experiments, yields were calculated using an internal standard such as biphenyl, DSS-Na and $DMSO_2$ with pulse delay larger than 10 s. Between NMR experiments or repeated heating cycles in an oil bath, samples were stored at 4 °C unless otherwise specified.

The enantiomeric excess (*ee*) was determined by using a Finnigan trace gas chromatograph ultra (Thermo Electron Corporation) equipped with a HP-CHIRAL-20B capillary column (30 m × 0.25 mm × 0.25 μm) with H_2 carrier gas. For the analysis, 10 μL of the reaction mixture was added to 1 mL methanol.

Stability of GVL at 150 °C

Dry GVL (8.60 mL) was placed in a 15-mL pressure glass tube and heated at 150 °C under air in an oil bath. Liquid samples (250 μL) were taken at different times and transferred to NMR tubes. After the addition of d_6-DMSO (250 μL), the mixtures were analyzed by NMR.



Scheme 4 The reaction of GVL with aqueous bases

Stability of GVL in the presence of water at 150 °C

A solution of GVL (10.56 mL) and H_2O (1.5 mL) was placed in a 15-mL pressure glass tube and heated at 150 °C under air in an oil bath. Liquid samples (250 μL) were taken at different times and transferred to NMR tubes. After the addition of a solution of 5 mg (0.023 mmol) 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS-Na) in 250 μL d_6-DMSO, the mixtures were analyzed by NMR.

Stability of GVL under aqueous acidic conditions at different acid concentrations

In 5 mm NMR tubes, GVL (1 mL, 10.5 mmol) was mixed with different concentrations of HCl (0.1 to 12 mol/L) or H_2SO_4 (0.1 to 14 mol/L) in amounts that the water contents of the mixtures were constant (0.15 g, 8.3 mmol). The final acid concentrations of the HCl and H_2SO_4 in solutions ranged from 0.02 to 2.0 mol/L and 0.01 to 4.05 mol/L, respectively. The NMR tubes were closed and taken for ^{1}H–NMR measurement immediately. Then, all tubes were stored at 23 °C and taken for ^{1}H–NMR measurement in every week.

Stability of GVL in the presence of 25% NH_4OH

A solution of 2.16 mL GVL (22 mmol) and 0.79 mL 25% NH_4OH (12 mmol NH_3) was stirred at room temperature for 15 h. Liquid samples (200 μL) were then taken and transferred to a NMR tube. After the addition of D_2O (300 μL), the mixture was analyzed by NMR. ^{1}H NMR of the reaction mixture showed peaks for H_2O, GVL (70%), 4-hydroxyvaleric amide (28%), and 4-hydroxyvaleric acid (2%) (Fig. S4).

A solution of 10.9 mL of GVL (109 mmol) and 54 mL 25% NH_4OH (820 mmol) was stirred at room temperature for 15 h. Liquid samples (200 μL) were then taken and transferred to a NMR tube. After the addition of D_2O (300 μL), the mixture was analyzed by NMR. ^{1}H NMR of the reaction mixture revealed the presence of 99.9% 4-hydroxyvaleric amide and 0.1% of GVL. The mixture was then distilled under vacuum (3.75 mmHg) at 69 °C resulting in 8.36 g distillate containing 99.7% of GVL and 0.3% 4-hydroxyvaleric amide.

Synthesis of (S)-GVL

The complete hydrogenation of 9.8 mmol levulinic acid was performed in the presence of 0.004 mmol of (*S*)-[(RuCl(SEGPHOS))$_2$(μ-Cl)$_3$][NH$_2$Me$_2$] in 1.46 mL methanol under 60 bar H_2 at 140 °C for 20 h [37]. (*S*)-GVL was separated by vacuum distillation (78–80 °C, 2 mmHg) and isolated as a colorless liquid (560 mg). Yield: 59.6%, *ee*: 78%.

Stability of (S)-GVL in the presence of water, aqueous HCl, and aqueous NaOH

A mixture of 0.3 μL (*S*)-GVL (ee = 78%) and 30 μL of an aqueous solution with carefully adjusted pH (between 1 and 13 using aqueous HCl or NaOH) was stirred at different temperatures (25, 50, 75, and 100 °C). After 24 h, 1 mL of EtOAc was added to the reaction mixture to form two phases. The upper organic phase was analyzed by chiral GC to establish the enantiomeric excess of the extracted (*S*)-GVL (Table S3).

Results and discussions

Dry GVL is stable at room temperature under air for a long time and remained stable at 150 °C for several days (Fig. S1). At much higher temperatures (>600 °C), GVL can undergo a ring-opening reaction to form the isomers of pentenoic acid followed by the formation of butenes and CO_2 and other decomposition products [13].

Although GVL does not react with water under neutral conditions at room temperature for 3 months and at 60 °C for 28 days [10], GVL and H_2O reaches an equilibrium with 4-HVA (Scheme 2) after several days at 150 °C (Fig. S2). The rather slow approach to the equilibrium is probably due to the combination of the high activation energy of the ring-opening reaction and the very low acidity of water [38]. Thus, when GVL is used as a solvent in chemical reactions in the presence of water (which is either in the reactants or formed during the reactions) at or above 100 °C, and the presence of 4-HVA has to be considered as a co-solvent or co-reagent.

The acid catalyzed hydrolysis of cyclic esters is well-known [39]. We have therefore investigated the ring-opening reaction with water in the presence of hydrochloric and sulfuric acids at room temperature. The acid concentrations of HCl and H_2SO_4 were varied between 0.02–2.0 mol/L and 0.01–4.05 mol/L, respectively; meanwhile, GVL and water were used at commeasurable quantities. In situ, NMR has revealed that at very high acid concentrations, only relatively small amount of 4-HVA is present in the equilibrium (Table S1). The presence of 4-HVA was confirmed by in situ COSY measurements (Fig. S3). This experimental observation can be initially rationalized by the following three equilibria competing for water:

$$\begin{gathered}
\mathrm{H}_n\mathrm{A} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{H_{n-1}A^-}(K_{\mathrm{a1}}) \\
\mathrm{H_{n-1}A^-} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + A^{2-}(K_{\mathrm{a2}}) \\
\mathrm{GVL} + \mathrm{H_2O} \rightleftharpoons \text{4-HVA}\left(K_{\mathrm{ring}}\right)
\end{gathered}$$

Since HCl and H_2SO_4 are both strong acids in presence of water, K_{a1} were set as 10^{10} and 10^8 for both. It should be noted that $K_{a2} = 0.0575$ was used in the case of sulfuric acid indicating that the dissociation of proton from HSO_4^- is not complete at large sulfuric acid concentrations. Having the equilibrium concentration of 4-HVA, K_{ring} was obtained by nonlinear parameter estimation performed by ZiTa [40], a comprehensive program package used for determining the kinetic parameters of a given model. During the course of the calculations, the relative average deviation is minimized between the measured and calculated 4-HVA concentrations by optimizing the value of K_{ring}. In the case of using the data obtained in the presence of HCl or H_2SO_4, the calculated K_{ring} was $(5.85 \pm 0.60) \times 10^{-3}$ and $(4.50 \pm 0.35) \times 10^{-3}$, respectively. The average deviation between the measured and calculated 4-HVA concentrations was 0.04 mol/L for HCl and 0.0374 mol/L for H_2SO_4. Since the highest measured 4-HVA concentration exceeded 0.4 mol/L, it estimates a more than 10% error of the concentration determination. This difference and the fact that the equilibrium constant of the ring-

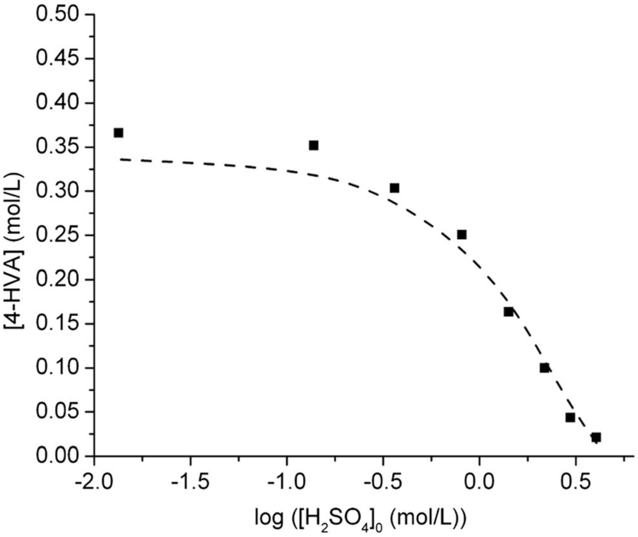


Fig. 1 Initial sulfuric acid concentration dependence of [4-HVA]. ■: experimental —: calculated

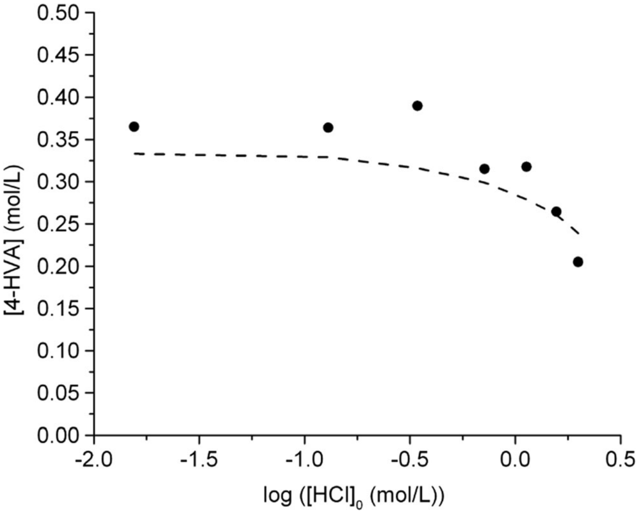
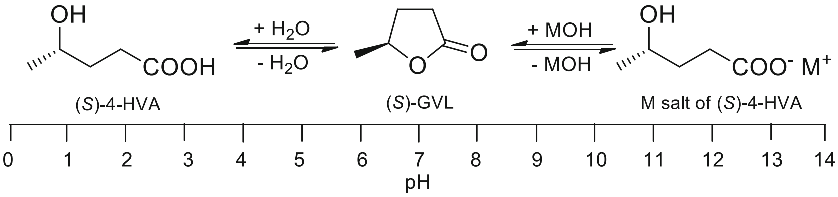


Fig. 2 Initial hydrochloric acid concentration dependence of [4-HVA]. ●: experimental —: calculated

Scheme 5. Reversible ring opening of (*S*)-GVL at different pH



opening reaction differs significantly, prompted us to improve the kinetic model. We have added the following two more equilibria into the previous system:

$$2\ H_2O \rightleftharpoons H_3O^+ + OH^- (K_3)$$
$$GVL + H_3O^+ \rightleftharpoons GVL^-H^+ + H_2O (K_4)$$

During the course of calculation $K_3 = K_w/[H_2O]^2 = 10^{-14}/55.55^2 = 3.24 \times 10^{-18}$ was fixed (at room temperature the ionization constant of water is approximately 10^{-14}) and the value of K_4 was fitted along with that of K_{ring}. As it was done before, the fitting procedure was performed first separately for different acids. Surprisingly, $K_{ring} = (5.62 \pm 0.20) \times 10^{-3}\ M^{-1}$ and $K_4 = (4.00 \pm 1.10) \times 10^{-4}$ were obtained if hydrochloric acid was used as a catalyst, while $K_{ring} = (5.38 \pm 0.15) \times 10^{-3}$ and $K_4 = (3.96 \pm 0.85) \times 10^{-4}$ were found in the case of using sulfuric acid as a catalyst. Thus, in the final calculation procedure, we used all the experimental data independently of the nature of the acid applied to obtain K_{ring} and K_4. These results suggest that indeed the ring-opening reaction is subject to general acid catalysis, so our final calculation procedure was executed using all experiments simultaneously. As a result of this calculation, we concluded that the value of $(5.57 \pm 0.18) \times 10^{-3}\ M^{-1}$ for the equilibrium constant of the ring-opening reaction of GVL at room temperature, meanwhile $K_4 = (3.5 \pm 0.1) \times 10^{-4}$. Figures 1 and 2 show an acceptable agreement between the measured and calculated data and provides a strong support of the model developed.

Since the reaction of GVL with water leads to an equilibrium with 4-HVA, we have also studied its reaction with ammonium hydroxide [23] to see if the formation of 4-hydroxyvaleric amide is reversible. ^1H NMR of the mixture of 21.6 mmol GVL and 12.0 mmol ammonia (using a 25% aqueous NH_4SO_4 solution) has shown the presence of 70% GVL, 28% 4-hydroxyvaleric amide, and 2% 4-HVA after stirring at room temperature for 15 h (Fig. S4). By increasing the ammonia/GVL ratio to 1.2, the concentration of GVL decreased to about 60% indicating that excess amount of ammonia was necessary to drive the reaction to "completion". Indeed, less than 1% GVL was present in the reaction mixture when the ammonia/GVL ratio was increased to 7.7 (Fig. S5). We have also noted that by heating the reaction mixture under vacuum, most of the GVL could be regenerated, as expected [41].

Enantiomerically pure GVL could be an excellent chiral building block in the synthesis of biologically active compounds and stability of its stereogenic center is crucial for this purpose. It was already demonstrated by the use of ^{18}O-isotope labeling technique that the reversible ring-opening reaction of GVL in the presence of 0.3 mol/L HCl has no effect on the stability of the chiral center [37]. The ring opening of the chiral GVL resulted in the formation of chiral 4-HVA, which then can subsequently be used to introduce the chiral center under either acidic or alkaline conditions. Consequently, we have investigated the stability of the chiral center between pH =1–13 and 25–100 °C. The chiral center of (*S*)-GVL (ee = 78%) remained unchanged when the aqueous solution of (*S*)-GVL was stirred at 25, 50, 75, and 100 °C for 24 h, as expected. Similar results were observed in the presence of different amount of HCl (pH =1–6) and NaOH (pH =8–13) at 25–100 °C. After the extraction of the reaction mixture with EtOAc, the chiral GC analysis of the organic phase established that the enantiomeric excess of the extracted (*S*)-GVL was 77 ± 1.75% (Table S1). While the formation of (*S*)-4-HVA was observed at acidic conditions, the (*S*) sodium salt of 4-HVA was formed at basic conditions (Scheme 5).

Conclusions

We have now shown that dry GVL is stable for several weeks at 150 °C and its thermal decomposition only proceed in the presence of appropriate catalysts. Since GVL does not react with water up to 60 °C for several weeks, it could be used as a green solvent at mild conditions. At higher temperatures, GVL reacts with water to form 4-HVA and the equilibrium can be reached in a few days at 100 °C. The establishment of the equilibrium should be even faster at higher temperatures, though the equilibrium should be shifted back towards HVA and water. Aqueous solutions of acids or bases catalyze the ring opening of GVL even at room temperature, which lead to the establishment of an equilibrium between GVL, water and 4-HVA. Although the 4-HVA concentration would be below 4 mol% in the presence of acids, it could be higher than the concentration of a reagent or a catalyst precursor, not to mention a catalytically active species. The latter could be especially worrisome as 4-HVA could be an excellent bi- or even a tridentate ligand for transition metals.

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