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Catalysts/cosolvents and general acid catalysts for acceleration of the hydrolysis of osmate(VI) esters

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ABSTRACT

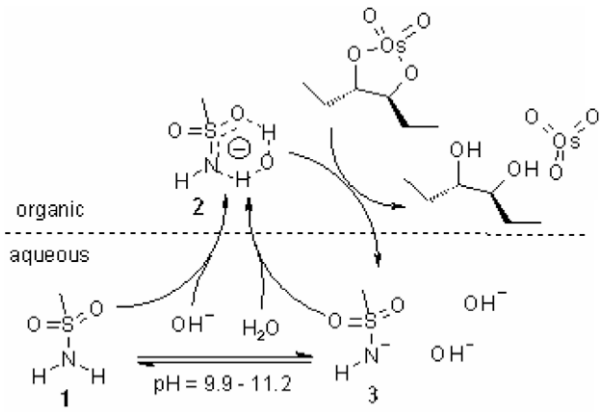
New catalysts/cosolvents as hydrolysis aids and the properties of the catalyst/cosolvent that effect the efficiency of the hydrolysis aid for the hydrolysis of osmate(VI) esters of aliphatic olefins are presented. Also, the effect of pH of the reaction media on the specific and general acid-catalysed hydrolysis of osmate(VI) esters of conjugated aromatic olefins is presented.

In Sharpless asymmetric dihydroxylation (AD) the rate limiting step is hydrolysis of the intermediate osmate(VI) esters.[1–3] Methanesulfonamide (**1**) is an additive that can accelerate the hydrolysis under the biphasic conditions typical for AD.[4] We have reported that the acceleration is due to two different effects: (1) (**1**) is a cosolvent that aids in the transfer of OH^- to the ^{t}BuOH phase in AD of aliphatic olefins and (2) (**1**) is a general acid catalyst in AD of conjugated aromatic olefins.[5]

We have described an interaction that delocalises the negative charge on OH^- efficiently such that a protic solvent such as ^{t}BuOH can dissolve it.[5] The additive **1** and OH^- form a six-membered ring structure **2** (Scheme 1), which is held together by hydrogen bonding and resonance. Under alkaline conditions the weakly acidic **1** exists in neutral and deprotonated form **3**. The latter forms structure **2** with H_2O. Thus, one could justifiably say that **3** is a catalyst. Water is not nucleophilic enough to react with the osmate(VI) ester, but when attached to **3**, it is sufficiently reactive to hydrolyse osmate(VI) esters.

The aim of this study was to find other compounds that could be used as catalysts/cosolvents to accelerate the hydrolysis step during AD. Compounds were chosen such that they met three criteria: (1) ability to form a similar structure to **2**, (2) are soluble in water and (3) possess a pK_a value close to that of **1**. The chosen compounds, succinimide (**4**), benzenesulfonamide (**5**), methanesulfonamide (**1**), *N*-methyl methanesulfonamide (**6**) and glutarimide (**7**), are presented below with their pK_a values.[6]

The catalyst/cosolvent effect was studied by determining the first-order rate constants of the ADs of *trans*-5-decene and 1-hexadecene.[7] Figure 1 shows the rate constants and initial $[OH^-]$ in ^{t}BuOH in the presence of **1**, **4**–**7** versus pK_a of the compounds.[8] Clearly, the reaction rates do not correlate linearly with either the pK_a values or the initial $[OH^-]$ in ^{t}BuOH. However, the initial $[OH^-]$ in ^{t}BuOH correlates with the acidity of the compound. Glutarimide (**7**), in our series of compounds, was the only one that decelerated the ADs of *trans*-5-decene and 1-hexadecene.[9]



Scheme 1. $CH_3SO_2NH_2$ and $CH_3SO_2NH^-$ as catalyst/cosolvent in the hydrolysis of aliphatic osmate(VI) esters.

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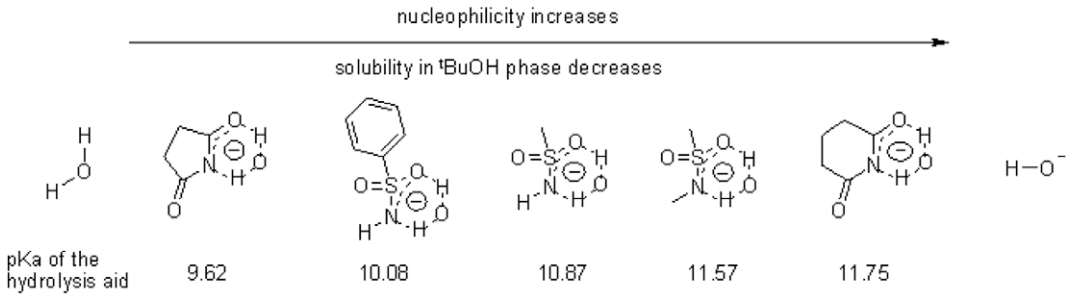


Scheme 2. Nucleophilicity of the catalyst/cosolvent-OH^- pair increases and the solubility in ^{t}BuOH decreases the less acidic the compound is.

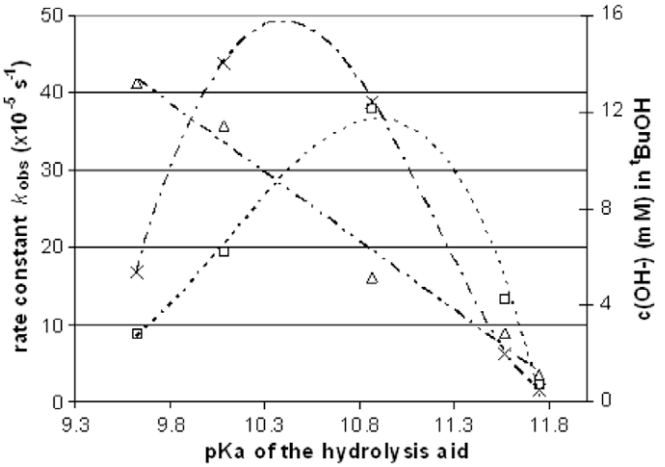


Figure 1. First-order rate constants of the ADs of *trans*-5-decene (×) and 1-hexadecene (□) and initial [OH^-] in ^{t}BuOH (△) in the presence of catalyst/cosolvent vs pK_a of the catalyst/cosolvent. Catalyst/cosolvent from left to right: succinimide, benzenesulfonamide, methanesulfonamide, *N*-methyl methanesulfonamide and glutarimide.

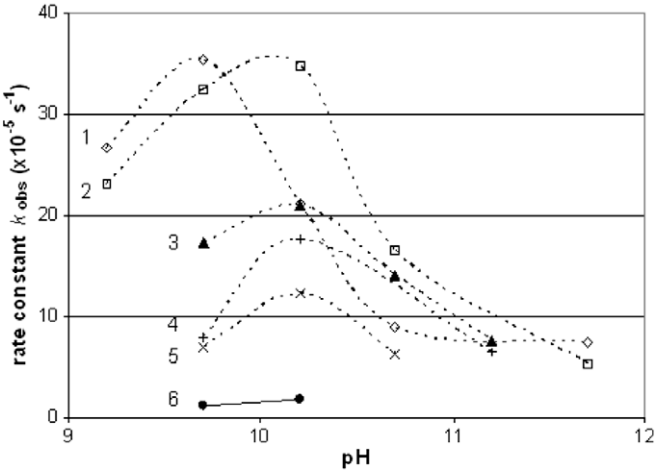
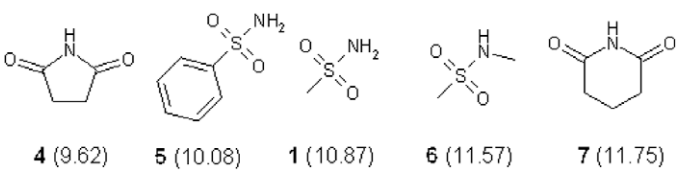


Figure 2. Pseudo-first-order rate constants of ADs of ethyl cinnamate in the presence of different additives versus pH of the reaction media: (1) no additive, (2) methanesulfonamide, (3) benzenesulfonamide, (4) glutarimide, (5) *N*-methyl methanesulfonamide, (6) succinimide.



4 (9.62) **5** (10.08) **1** (10.87) **6** (11.57) **7** (11.75)

Delocalisation of the negative charge in the catalyst/cosolvent-OH^- pair influences the reactivity of the ion-pair in two ways as presented in Scheme 2. The more acidic the compound is, the more efficient is the delocalisation of the negative charge in the ion-pair. Efficient delocalisation leads to better solubility in ^{t}BuOH. On the other hand, efficient delocalisation decreases the nucleophilicity of the ion-pair. Thus, in the presence of the strongest acid the initial [OH^-] is highest in ^{t}BuOH; however, the reaction is slower than the AD in the presence of some weaker acids (Fig. 1).

It is expected that the more hydrophobic the catalyst/cosolvent-OH^- pair is, the more soluble in ^{t}BuOH it would be; however, this seems not to be the case. The *c* log *P* values of the compounds we used are: −1.184 (**4**), 0.326 (**5**), −1.287 (**1**), −0.952 (**6**) and −0.039 (**7**).[10] Compounds **5** and **7** are the most hydrophobic, but the [OH^-] in ^{t}BuOH in the presence of **5** is ten times the [OH^-] in the presence of **7** as presented in Figure 1. Sulfonamide **6** is almost as hydrophilic as **4**, yet the [OH^-] in ^{t}BuOH in the presence of **6** is almost one third of the [OH^-] in the presence of **4**. The acidity of the compound seems to be the major factor in determining the solubility of the ion-pair in ^{t}BuOH.

We have reported that the hydrolysis of osmate(VI) esters of conjugated aromatic olefins can be specific acid catalysed, or in the presence of **1**, general acid catalysed.[5,11] Figure 2 presents the pseudo-first-order rate constants of the ADs of ethyl cinnamate without and in the presence of various additives under different alkaline conditions.[12] The rate acceleration at a pH of about 10.7 indicates that hydrolysis of the osmate(VI) ester of ethyl cinnamate without catalyst becomes specific acid catalysed below that pH (line 1, Fig. 2). The reaction is also most likely a concerted process, that is, protonation and OH^- attack on the osmate–ester group are concurrent, since rate deceleration is observed below pH 9.7. Similar trends were observed in ADs of ethyl cinnamate in the presence of the other sulfonamides (lines 2, 3 and 5, Fig. 2). The major difference is that in the presence of sulfonamides, hydrolysis is a general acid-catalysed concerted process.

Succinimide (**4**) is the strongest acid in our series of compounds, yet the AD of ethyl cinnamate was by far the slowest in the presence of **4** (line 6, Fig. 2). A plausible explanation is that the proton in **4** is so shielded that it cannot protonate osmate(VI) esters and the reaction takes place via a specific acid-catalysed concerted pathway. The (**4**)-OH^- pair is a weak nucleophile and, therefore, the reaction is slow. Glutarimide (**7**) is a weaker acid than **4**; however, the AD of ethyl cinnamate in the presence of **7** is faster (line 4, Fig. 2). The (**7**)-OH^- pair is a stronger nucleophile than the (**4**)-OH^- pair, therefore, the specific acid-catalysed concerted reaction in the presence of **7** is faster.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.04.116.

References and notes

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5. Junttila, M. H.; Hormi, O. E. O. *J. Org. Chem.* **2009**, *74*, 3038–3047.
6. pK_a values are predicted values from SciFinder.
7. *Procedure for determining the first-order rate constants*: A 50 mL three-necked flask was charged with 1 mmol of olefin, 7.7 mg (0.1 mmol, 1 mol %) of ligand $(DHQD)_2PHAL$, 0.414 g (3 mmol) of K_2CO_3 and 0.990 g (3 mmol) of $K_3[Fe(CN)_6]$. The amount of **1**, **4**, **5**, **6** or **7** was 1 mmol. Reagents were dissolved in 10 mL of $^tBuOH/H_2O$ (1:1) mixture. The reactions were initiated by adding 1.5 mg (0.04 mmol, 0.4 mol %) of $K_2OsO_4{\cdot}2H_2O$. The reactions were performed at room temperature and were monitored by following the consumption of olefin. Aliquots of 20 μL were withdrawn from the reaction mixture after allotted periods of time. The reaction was quenched by diluting the sample with a mixture containing 20 μL of a 60 mM solution of Na_2SO_3 and 200 μL of 0.01 M 1-phenylethanol (standard) in EtOAc. The sample was dried over Na_2SO_4 prior to analysis by GC.
8. Initial $[OH^-]$ in the presence of **1**, **4**, **5**, **6** or **7** was analysed by titrating a diluted sample from ^tBuOH with oxalic acid.
9. The first-order rate constants of the ADs of *trans*-5-decene and 1-hexadecene without catalyst/cosolvent were $3.14 \times 10^{-5}\ s^{-1}$ and $5.45 \times 10^{-5}\ s^{-1}$.
10. *c* log *P* values are predicted values from SciFinder.
11. Junttila, M. H.; Hormi, O. E. O. *J. Org. Chem.* **2007**, *72*, 2956–2961.
12. The procedure was the same as that for determining the first-order rate constants in ADs of *trans*-5-decene and 1-hexadecene except that the pH was adjusted with $NaHCO_3$ to a certain level and kept constant by adding 8 M NaOH to the reaction mixture.