Journal of Molecular Catalysis A: Chemical 326 (2010) 15–20

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Editor's Choice paper

Catalysis of redox isomerization of allylic alcohols by $[RuClCp(mPTA)_2](OSO_2CF_3)_2$ and $[RuCp(mPTA)_2(OH_2\text{-}\kappa O)](OSO_2CF_3)_3\cdot(H_2O)(C_4H_{10}O)_{0.5}$. Unusual influence of the pH and interaction of phosphate with catalyst on the reaction rate

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ARTICLE INFO

Article history:
Received 7 March 2010
Received in revised form 9 May 2010
Accepted 11 May 2010
Available online 20 May 2010

Keywords:
Allylic alcohols
Redox isomerization
Phosphate coordination
Ruthenium
Methyl-PTA

ABSTRACT

In aqueous solutions at 80 °C, $[RuClCp(mPTA)_2](OSO_2CF_3)_2$ (**1**) and $[RuCp(mPTA)_2(OH_2\text{-}\kappa O)](OSO_2CF_3)_3\cdot(H_2O)(C_4H_{10}O)_{0.5}$ (**3**) (mPTA: *N*-methyl-PTA) were found effective catalysts of the redox isomerization of alk-1-en-3-ols to the corresponding ketones, characterized by initial turnover frequencies (TOF) of 162 h^{-1} (**3**) and 9.6 h^{-1} (**1**) in 1-octen-3-ol isomerization. A sharp maximum of the reaction rate as a function of pH was observed with **1** in phosphate buffer solutions. Kinetic and ^{31}P NMR measurements revealed for the first time in aqueous organometallic catalysis that component(s) of phosphate buffer (most probably HPO_4^{2-}) strongly interact(s) with the catalyst complexes and this interaction leads to a dramatic loss of the catalytic activity.

1. Introduction

Water is an environment-friendly solvent for organic reactions and for that reason it has attracted increasing interest recently both from industrial and academic viewpoints [1–4]. The most common and efficient catalysts in aqueous media are transition metal complexes containing water-soluble phosphines, such as the monosulfonated and trisulfonated triphenylphosphines, usually as their sodium salts (*m*tppms-Na [5,6] and *m*tppts-Na_3 [7,8], respectively). In addition to sulfonated tertiary phosphines, the water-soluble aliphatic caged phosphine PTA (1,3,5-triaza-7-phosphatricycle[3.3.1.1^{3,7}]decane or 1,3,5-triaza-7-phosphaadamantane) [9,10] and its various derivatives have often been used for the synthesis of water-soluble organometallic complexes. A wide range of water-soluble homogeneous catalysts containing rhodium, ruthenium, palladium, iridium, and other metal ions has been reported [1–14].

Catalytic isomerization of allylic alcohols (*e.g.* Scheme 1) is an attractive strategy for the synthesis of the corresponding ketones (and aldehydes) [15–17]. Such internal redox reactions (transpositions) show 100% atom economy and therefore much effort has been spent on the study of these processes following the seminal works of Blum and co-workers [18] and Trost and Kulawiec [19].

In most previous investigations, isomerization processes have been studied in organic solvents, such as THF [20,21] and alkanes [22]. Very efficient catalyst systems were developed based on ruthenium complexes [23–29] with a turnover frequency (TOF) as high as 62500 h^{-1} [TOF = (mol converted substrate)(mol catalyst)$^{-1}h^{-1}$] [26]. Several of these catalysts are catalytically active in aqueous or aqueous-organic biphasic systems, too [24–29]. In addition to tertiary phosphine-containing catalysts, a few complexes with N-heterocyclic carbene ligands were also used as catalysts of redox isomerization of allylic alcohols in aqueous media [30,31].

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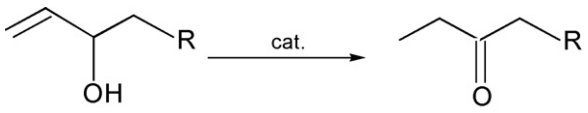
doi:10.1016/j.molcata.2010.05.003



Scheme 1. Isomerization of alk-1-ene-3-ols.

Ruthenium(II) complexes of PTA and its derivatives have been widely used recently as water-soluble catalysts of hydrogenation [32], hydroformylation [33], and hydrogen transfer [34] reactions as well as promising compounds of anticancer activity [35,36].

Some of us have reported earlier the synthesis of [RuClCp(mPTA)$_2$](OSO$_2$CF$_3$)$_2$ (**1**) and its reactions in aqueous solutions to yield – inter alia – [RuCp(OH-κ*O*)(mPTA)$_2$](OSO$_2$CF$_3$)$_2$·(C$_4$H$_{10}$O) (**2**) and [RuCp(mPTA)$_2$(OH$_2$-κ*O*)](OSO$_2$CF$_3$)$_3$·(H$_2$O)(C$_4$H$_{10}$O)$_{0.5}$ (**3**) where mPTA: *N*-methyl-PTA [37,38]. Here we report the results of the investigation of **1** and **3** as catalysts (precursors) in the redox isomerization of enols in aqueous solutions or in aqueous-organic biphasic systems. A large effect of the solution pH on the reaction rates was observed together with a remarkable influence of phosphate buffer on catalysis; the general consequences of such interactions in aqueous organometallic catalysis is also discussed.

2. Experimental

2.1. Materials and equipment

[RuClCp(mPTA)$_2$](OSO$_2$CF$_3$)$_2$ (**1**), [RuCp(mPTA)$_2$(OH$_2$-κ*O*)](OSO$_2$CF$_3$)$_3$·(H$_2$O)(C$_4$H$_{10}$O)$_{0.5}$ (**3**) [37], PTA [39] and mPTA (triflate salt) [40] were synthesized according to published procedures. All other reagents were obtained from Sigma–Aldrich-Fluka and Lancaster and used without further purification.

All reactions and manipulations were routinely performed under an atmosphere of dry nitrogen or argon using vacuum-line and standard Schlenk techniques. Solvents were dried and deoxygenated under nitrogen/vacuum before use. Doubly distilled water was used throughout. Gas chromatographic measurements were made on a Hewlett-Packard HP 5890 Series II equipment using a Varian CP-Wax 52 CB, 30 m, 0.32 mm, 0.25 μm (CP884) column and FID and on a Varian (Walnut Creek, CA, USA) CP-3380 GC gas chromatograph equipped with a 1177 split/splitless injector (250 °C), Factor Four VF23 capillary column and flame ionization detector (280 °C). The elution was performed in split mode (1/20 split ratio), isothermal at 80 °C and nitrogen as carrier gas at 1 mL/min. NMR spectra were recorded on a Bruker AVANCE DRX300 spectrometer operating at ca. 300 MHz (^{1}H) and ca. 75.4 MHz (^{13}C), respectively. Peak positions are reported relative to tetramethylsilane calibrated against the residual solvent resonance (^{1}H) or the deuterated solvent multiplet (^{13}C). ^{31}P{^{1}H} NMR spectra were recorded on the same instrument operating at ca. 121 MHz. Chemical shifts were measured relative to external 85% H$_3$PO$_4$ with downfield values taken as positive.

2.2. General procedure for catalytic isomerization of allylic alcohols

1.74 mL of deoxygenated solvent (water, Na-phosphate or citrate buffer of appropriate pH) was introduced into a Schlenk tube. After closing, the air was removed from the tube by several evacuation/refill (Ar) cycles. Then the catalyst precursor (0.1–4 mol%), and the allylic alcohol (1 mmol) were added under an argon atmosphere. In some experiments 3 mL of the aqueous phase and 1.5 mL of toluene as the organic phase were used. The tube was placed into a water bath the temperature of which was controlled by a Julabo F25 circulator. The reaction was started by starting the magnetic stirring. After the required time the resulting mixture was cooled to room temperature and extracted by CHCl$_3$, filtered through MgSO$_4$ and analyzed by gas chromatography. The identity of the products was established by comparison with commercially available pure samples. The conversion of allyl alcohol was determined by ^{1}H NMR spectroscopy.

Table 1
Isomerization of various allylic alcohols catalyzed by [RuClCp(mPTA)$_2$](OSO$_2$CF$_3$)$_2$ (**1**).

Substrate	Conversion (%)	TOF (h^{-1})
Oct-1-en-3-ol	50	18.7
Hept-1-en-3-ol	28	10.0
Hex-1-en-3-ol	20	7.1
Pent-1-en-3-ol	20	7.1
But-1-en-3-ol	17	6.1
2-Methylprop-2-en-1-ol	27	9.6
Prop-2-en-1-ol	0	0

Conditions: 1 mmol substrate, 12 mg catalyst (0.014 mmol), 3 mL 0.1 M phosphate buffer, pH 4.75, 2 h reaction time, 80 °C.

2.3. Reaction of **3** in H_2O with NaCl at 25 and 80 °C

In a 5 mm NMR tube containing 0.5 mL of H$_2$O was dissolved **3** (10 mg, 0.012 mmol) and 5 equivalents of NaCl (3.5 mg, 0.6 mmol). The ^{31}P{^{1}H} NMR at room temperature showed the exclusive presence of **1** (δ = −10.77 ppm) which remained the unique detected compound at 80 °C.

2.4. Study of the behaviour of **3** in H_2O at 25 and 80 °C

Compound **3** (10 mg, 0.012 mmol) was dissolved in 0.5 mL of H$_2$O in a 5 mm NMR tube. The ^{31}P{^{1}H} NMR spectra evolved from −10.61 ppm at room temperature to a broad signal at −10.50 ppm which returned to the original signal when temperature was reduced to 25 °C.

2.5. Study of the behaviour of 3 in 0.1 M phosphate buffer at pH of 4.75 (25, 80 °C)

Into a 5 mm NMR tube was introduced 3 (10 mg, 0.012 mmol) and 0.5 mL of a 0.1 M phosphate buffer of pH 4.75. The ^{31}P{^{1}H} NMR spectrum obtained after 5 min at room temperature showed signals at 8.64 ppm (2.50%; broad), 0.66 ppm (60.93%; broad; phosphate), −5.32 ppm (0.91%; broad), −8.95 ppm (3.77%; broad) and −10.58 ppm (31.90%) which did not change during 2 h. At 80 °C the observed signals were at 9.13 ppm (3.52%; broad), 1.23 ppm (72.91%; broad; phosphate), −3.63 ppm (0.76%; broad), −8.52 ppm (4.22%; broad) and −10.45 ppm (18.59%), and were not significantly changed after 2 h at this temperature. The sample was let to cool and the spectrum recorded newly at room temperature showed the same signal pattern what was previously observed at this temperature.

3. Results and discussion

We have found that on the catalytic action of [RuClCp(mPTA)$_2$](OSO$_2$CF$_3$)$_2$ (**1**) at 80 °C several enols with the notable exception of allylic alcohol were selectively isomerized to the corresponding ketones with turnover frequencies in the range of 6.1–18.7 h^{-1} (Table 1).

The catalytic properties of **1** were studied in detail in the reaction of 1-octen-3-ol, as a representative example of the redox isomerization of allylic alcohols. Some of the reactions were carried out in the mixture of neat oct-1-en-3-ol with the aqueous solvent and the progress of the reaction was determined upon termination of

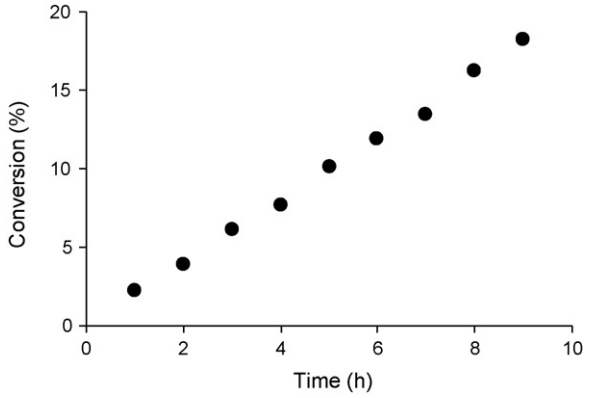


Fig. 1. Isomerization of oct-1-en-3-ol catalyzed by **1** as a function of time. *Conditions*: 12 mg catalyst (0.014 mmol), 160 μL oct-1-en-3-ol (1 mmol), 3 mL 0.1 M phosphate buffer, pH 4.75, 1.5 mL toluene, 80 °C.

the process by extraction with chloroform followed by GC analysis. Other reactions were run in biphasic mixtures of the aqueous buffer and toluene; by sampling the organic phase we could conveniently follow these reactions. However, since in these cases where the substrate was applied in dilute toluene solutions in the biphasic reaction mixtures, the reactions proceeded less rapidly than without toluene in the organic phase.

The reaction shows no induction period and at low conversions the yield of 3-octanone is a linear function of time (Fig. 1). Increasing the amount of the substrate in the organic phase results in lowering of the overall conversion, nevertheless the yield of 3-octanone produced in 2 h reactions varies according to a saturation curve upon the increase of substrate concentration (Fig. 2). The reaction rate (2 h conversions) shows a linear dependence on the catalyst concentration (see Supplementary Material). The effect of temperature on the conversion in the 40–80 °C range is surprisingly linear (see Supplementary Material) what may be the result of the different temperature sensitivity of the various chemical and physical processes (including *e.g.* mass transfer between phases) and of that of the isomerization reaction itself. It is emphasized that these measurements were done with 0.1 M phosphate buffer of pH 4.75 as the aqueous phase.

A striking feature of the reaction is that its rate shows a pronounced maximum as a function of the pH of the aqueous phase (Fig. 3). Under the conditions of Fig. 3, maximum conversion (50%) was observed at pH 4.75, and both in more acidic and more basic solutions the catalytic activity of **1** dropped sharply. Therefore in

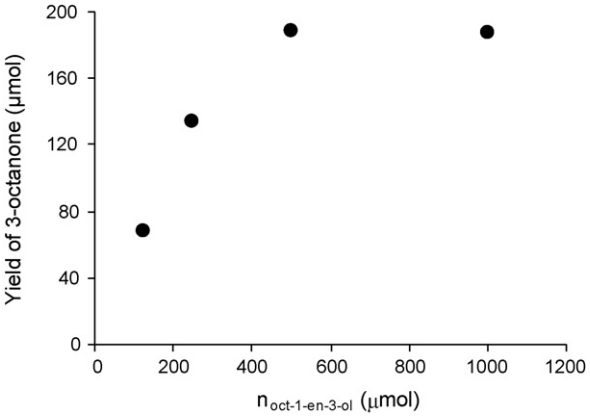


Fig. 2. Isomerization of oct-1-en-3-ol catalyzed by **1** as a function of amount of substrate. *Conditions*: 12 mg catalyst (0.014 mmol), 3 mL 0.1 M phosphate buffer, pH 4.75, 2 h reaction time, 80 °C.

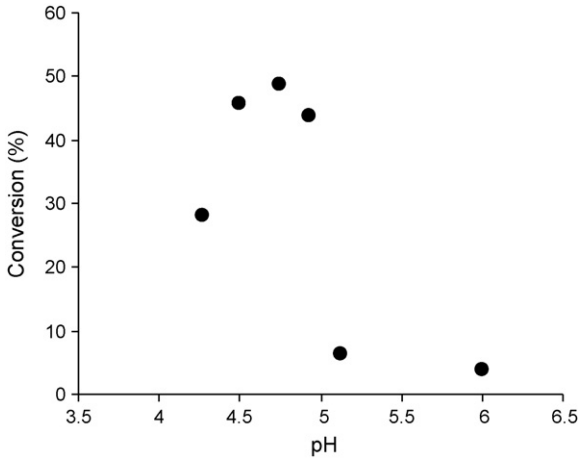


Fig. 3. Isomerization of oct-1-en-3-ol catalyzed by **1** as a function of pH. *Conditions*: 12 mg catalyst (0.014 mmol), 160 μL oct-1-en-3-ol (1 mmol), 3 mL 0.1 M phosphate buffer, 2 h reaction time, 80 °C.

most of the further studies the pH of the reaction mixture was adjusted to 4.75.

These observations are consistent with an η^3-oxo-allyl mechanism of the isomerization of enols to ketones [17]. According to this mechanism the substrate enol coordinates as a bidentate enolate with a concomitant *deprotonation*, while the isomerized product is liberated by *protonation* of the η^3-oxo-allyl intermediate. In principle, the balance of these two processes may lead to a maximum in the reaction rate at a particular pH.

In addition to the direct role of proton in the reaction mechanism of a catalytic transformation, the reaction rate can also be influenced by the pH through its effect on the composition or structure of the catalyst. In the 2.8–11.0 range, pH-potentiometric titration of **1** did not reveal a proton consuming or releasing process involving the complex. (This also means that the coordinated mPTA ligand is not protonated at pH ≥ 2.8 so this process cannot be involved in the pH dependence of the rate of catalytic redox isomerization of oct-1-en-3-ol.) UV–vis spectrophotometric and $^{31}P\{^1H\}$ NMR measurements indicated reversible reactions of **1** in strongly basic solutions (between pH 11 and 13); unfortunately these were not definitive with respect to the composition of the new species. Besides, the changes in such strongly alkaline solutions do not have relevance for the explanation of the rate changes around pH 5.

It is known from our previous studies [37,38] that the chloride ligand in $[RuClCp(mPTA)_2](OSO_2CF_3)_2$ (**1**) is replaced by hydroxyde in strongly alkaline aqueous solutions yielding $[RuCp(OH\text{-}\kappa O)(mPTA)_2](OSO_2CF_3)_2\cdot(C_4H_{10}O)$ (**2**). However, dissociation of chloride was not observed in water at room temperature, and the corresponding aqua-complex $[RuCp(mPTA)_2(OH_2\text{-}\kappa O)](OSO_2CF_3)_3\cdot(H_2O)(C_4H_{10}O)_{0.5}$ (**3**) could be prepared only via chloride abstraction by AgOTf (OTf: OSO_2CF_3). Complex **3** is stable in aqueous solutions and can be deprotonated by NaOH to yield **2**. In contrast to **1**, the closely related complex $[RuClCp(PTA)_2]$ is extensively dissociated ($K_{eq} = 6.18 \times 10^{-4}$) to yield $[RuCp(PTA)_2(H_2O)]^+$ in aqueous solutions already at room temperature [41]. The less closer analog $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2(PTA)]$ (*p*-cymene: 4-isopropyltoluene) readily looses both of its Cl^- ligands upon dissolution in water at 25 °C [42]. The lack of chloride dissociation from **1** at room temperature may be the consequence of the fact that the resulting species **3** is a tripositive ion. Nevertheless we reasoned that at the reaction temperature of oct-1-en-3-ol isomerization (80 °C), complex **3** may be present in the reaction mixture in substantial quantities and therefore we studied the redox isomerization of oct-1-en-3-ol with **3**, too, as catalyst. Furthermore,

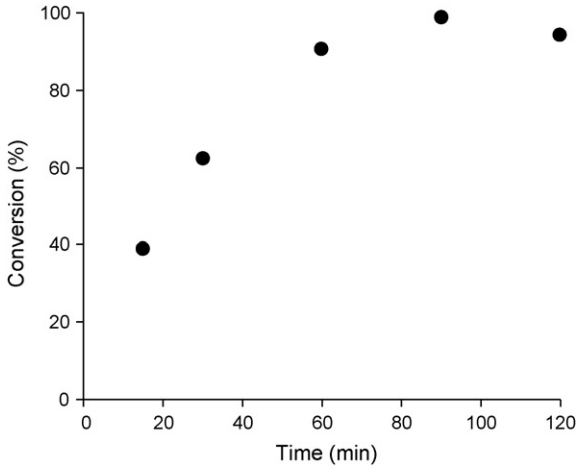


Fig. 4. Isomerization of oct-1-en-3-ol catalyzed by 3 as a function of time. *Conditions*: 5.2 mg catalyst (0.005 mmol), 80 μL oct-1-en-3-ol (0.5 mmol), 1.74 mL water, 80 °C.

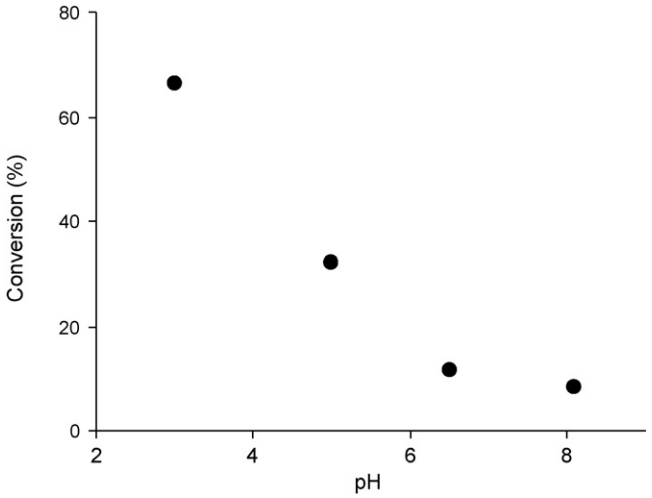


Fig. 5. Isomerization of oct-1-en-3-ol catalyzed by **3** in phosphate buffer as a function of pH. *Conditions*: 5.2 mg catalyst (0.005 mmol), 80 μL oct-1-en-3-ol (0.5 mmol), 1.74 mL 0.1 M phosphate buffer, 1 h reaction time, 80 °C.

$^{31}P\{^{1}H\}$ NMR spectra of **1** and **3** were recorded as a function of temperature both in the absence and in the presence of phosphate.

The compound 3-octanone was efficiently obtained in a biphasic mixture of water and neat oct-1-en-3-ol catalyzed by **3** (Fig. 4). In fact, the reactions catalyzed by **3** in water were much faster than with **1** in phosphate buffer as catalyst. At 80 °C, the initial TOF (calculated from conversions at 15 min) was as high as 162 h^{-1}, and TOF-s calculated from conversions belonging to 1 h reaction times were in the range of 85–100 h^{-1} in the case of higher substrate amounts (in the range of [catalyst]/[substrate] ratio 100–320).

Under the same conditions, hept-1-en-3-ol and pent-1-en-3-ol were similarly converted to the corresponding ketones with high efficiency (TOFs at 1 h: 99 and 89 h^{-1}, respectively; Table S1 in Supplementary Material). Large substrate loadings were also possible with **3** albeit requiring longer reaction times for high conversion; with a substrate/catalyst ratio of 1000, 93% conversion was reached in 20 h (Table S2 in Supplementary Material). It is interesting to note that **3** could be used in the presence of air, as well, with no apparent drop in catalytic activity. This is an important practical aspect, however, it was not investigated in detail.

Similar to the case of **1**, the rate was found to be a linear function of temperature in the range of 50–80 °C (see Supplementary Material). However, the reaction rate decreased monotonously upon raising the pH from 3.0 to 8.2 by using Na-phosphate solutions to set the desired pH (Fig. 5) which contrasts the findings with **1** as shown earlier in Fig. 3. The presence of phosphate had a detrimental effect on the reaction rate: under comparable conditions (pH 6.5), instead of 90% conversion obtained using water as solvent only 12% conversion to 3-octanone was determined using the same catalyst, **3**, but in phosphate buffer.

The finding that **3** is a much better catalyst than **1** for the redox isomerization of oct-1-en-3-ol is in agreement with the generally assumed need for a free coordination site to allow the interaction between the substrate and catalyst. In the case of **3**, an *O*-coordinated ligand (H_2O) has to be replaced by the κ*O*-substrate (assuming an η^3-oxo-allyl mechanism) and this step may take place with a low activation barrier. In addition, the observations strongly refer to an interaction of the catalyst with component(s) of the phosphate buffer. Therefore, we determined the effect of the pH on the rate of oct-1-en-3-ol isomerizations with catalyst **1** using citrate buffer instead of phosphate. In the pH range 3.7–5.7, where a sharp maximum of the rate was observed with phosphate, the use of citrate buffer as the aqueous phase led to monotonously decreasing conversions of low values (5–25%, Fig. 6). Although a specific interaction of citrate and **1** cannot be excluded, this finding allows the conclusion that it is the interaction of **1** and phosphate what is manifested in the maximum curve dependence of the conversions on pH in the range of 4.0–6.0.

Dissolved in H_2O at 25 °C, **1** displayed a single sharp $^{31}P\{^{1}H\}$ NMR signal at −10.77 ppm. However, increasing the temperature to 80 °C led to the shift of this resonance to −10.33 ppm, and to the appearance of several other weak signals of which the ones at −9.93 and −9.62 ppm were clearly discernible. When the solution was cooled back to 25 °C, all changes reverted and only the singlet at −10.77 ppm was observed indicating a complete reversibility of the process. These changes can be attributed to chloride dissociation from **1**, since in the presence of chloride the original singlet resonance at −10.77 ppm remained unchanged. When sufficient amounts of Na_2HPO_4 and NaH_2PO_4 were added to set the pH at 5.0, a strong singlet was seen at room temperature at −10.77 ppm (referring to **1** still being the major species, present in approximately 65% at this temperature), accompanied by weak singlets at −10.61 ppm (sharp) and at −9.74 ppm (broad). Most strikingly, upon heating the solution to 80 °C, only a sharp singlet was observed at −10.58 ppm with no additional weak signals.

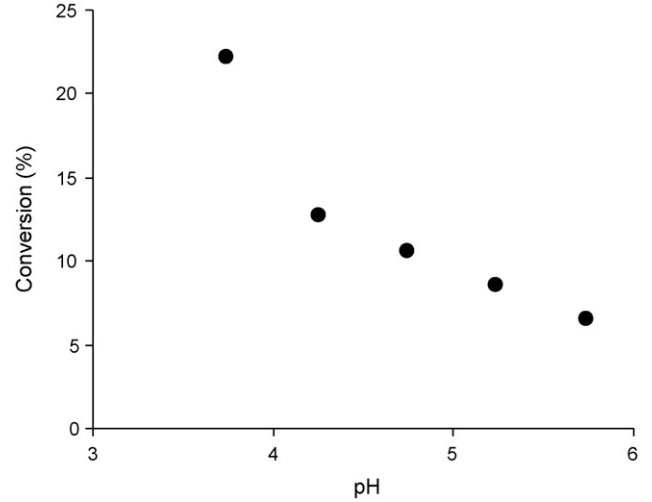


Fig. 6. Isomerization of oct-1-en-3-ol catalyzed by **1** in citrate buffer as a function of pH. *Conditions*: 12 mg catalyst (0.014 mmol), 160 μL oct-1-en-3-ol (1 mmol), 3 mL 0.1 M citrate buffer, 2 h reaction time, 80 °C.

According to these data, the molecular state of the Ru(II)-complex in phosphate buffer is clearly different from that in water both at 25 and 80 °C.

Similar to **1**, **3** was also found to be stable in aqueous solutions both at room temperature and at 80 °C (see Section 2). On the addition of phosphate buffer (pH 4.75), the singlet at −10.61 ppm ($^{31}P\{^1H\}$ NMR) observed at room temperature for **3** was shifted to −10.58 ppm, and weak singlets at 8.64 ppm, −5.32 ppm, and −8.95 ppm were also displayed. These signals showed small and reversible shifts upon heating the sample to 80 °C and then cooling it back to room temperature (see Section 2 and Supplementary Material).

The interaction of phosphate buffer with the analogous [Ru(η^6-*p*-cymene)Cl_2(PTA)] has been noted by Dyson et al. The UV–vis spectrum of this compound was essentially the same in water and in phosphate buffer of pH 2 (showing the presence of [Ru(η^6-*p*-cymene)Cl(H_2O)(PTA)]$^+$), while at pH 7 it was different and coincided with that recorded at pH 12; that was considered as "indicating that the phosphate interacts with the complex" [36,42].

In aqueous solutions the pK_a values of phosphoric acid are 2.14, 7.20, and 12.34 [43,44], therefore in the pH range of 4.50–5.00, where the maximum rate of isomerization is observed, $H_2PO_4^-$ is the dominant species with a mole fraction >99%. However, the mole fraction of HPO_4^{2-} increases exponentially above pH 5. Its concentration in 0.1 M phosphate buffer solutions at pH 6.00 reaches 5.93 mM which is in the range of the usual catalyst concentrations (2.7–4.7 mM) in this study. Strong interaction of the dinegative HPO_4^{2-} with the di- or tripositive ions of **1** or **3** may lead to poisoning of the catalyst.

The interaction of **1** or **3** with HPO_4^{2-} can explain the sharp drop of catalytic activity between pH 5 and 7. Note that albeit the concentration of $H_2PO_4^-$ is rapidly decreasing in this pH range, its actual concentration in the 0.1 M phosphate buffer (61.3 mM at pH 7.00) is still much higher than that of the catalyst. Consequently, if there was any interaction between the catalyst and $H_2PO_4^-$ (it should be beneficial, anyway, since the rate maximum is observed at a pH where the concentration of $H_2PO_4^-$ is at its maximum) it would probably not contribute to the overall change in the rate of isomerization. Deprotonation of [RuCp(mPTA)$_2$(H_2O-κ*O*)]$^{3+}$ requires addition of NaOH [37] so it is unlikely to proceed in such mildly acidic or neutral solutions and therefore it is unlikely to contribute to the changes in the reaction rate.

There are not many catalysts of redox isomerization in aqueous systems that can be compared to **1**. The complex Na_2[RuClCp(*m*tppms)$_2$] [45] is an analogous water-soluble half-sandwich complex of ruthenium. This compound showed excellent catalytic activity (up to TOF = 2200 h^{-1}) in the isomerization of oct-1-en-3-ol at 80 °C using 0.1 M phosphate buffer [27]. However, in acidic solutions, the reaction rate was only slightly effected by changes in the pH: the catalytic activity (TOF) of this catalyst diminished only slightly from 2200 h^{-1} (pH 2.2) to 2000 h^{-1} (pH 5.0) and only in more basic solutions could be a sharp drop of the catalytic activity observed (TOF 690 h^{-1} at pH 7.0).

Na-phosphate buffers are widely used as solvents in aqueous organometallic catalysis [1–4], however, so far no specific salt effect of phosphate on the catalytic activity or selectivity has been described in the literature. Conversely, in bioinorganic/bioorganometallic chemistry interactions of phosphate buffer with aquated Cisplatin [46] and [Ru(η^6-*p*-cymene)Cl_2(PTA)] [36,40] were clearly recognized, although the structures of the several resulting phosphate-containing species could not be fully determined. Our results unambiguously show that the species present in varying concentrations in phosphate buffers at various pH may interact with the catalytically active metal complexes and can strongly influence the catalytic properties of the latter.

4. Conclusion

Both [RuClCp(mPTA)$_2$](OSO_2CF_3)$_2$ (**1**) and [RuCp(mPTA)$_2$(OH_2-κ*O*)](OSO_2CF_3)$_3$·(H_2O)($C_4H_{10}O$)$_{0.5}$ (**3**) actively catalyzed the redox isomerization of alk-1-en-3-ols to the corresponding ketones in aqueous solutions or in aqueous-organic biphases at 80 °C with **3** being considerably more active than **1**. The catalytic activity of **1** dissolved in phosphate buffer showed a pronounced maximum at around pH 4.75. In contrast, the catalytic activity of **3** at this pH was largely diminished by phosphate buffer (compared to water as solvent) and decreased further monotonously with increasing pH. Based on kinetic and NMR measurements, it is concluded that components of phosphate buffer (first of all $H_2PO_4^-$ and HPO_4^{2-}) strongly interact with the dipositive and tripositive complex ions of **1** and **3**. Similar interactions were already noticed in bioinorganic/bioorganometallic chemistry, however, those are reported here for the first time for aqueous organometallic catalysis. The findings stress that although the use of buffers is essential in aqueous organometallic catalysis, and Na-phosphate buffers have been used frequently, their innocence cannot be taken for granted with all catalysts and must be scrutinized in all mechanistic investigations.

Acknowledgement

Funding provided by Junta de Andalucía through PAI (research teams FQM-317) and Excellence Projects FQM-03092, MCYT (Spain) by project CTQ2006-06552/BQU and the COST Action CM0802 (WG2, WG3, WG4), the Hungarian-Spanish Intergovernmental Collaboration in Science and Technology (TéT E-10/2005; HH2005-0001) and the Hungarian National Research and Technology Office - National Research Fund (NKTH-OTKA K 68482 and OTKA IN 78040). We acknowledge Dr. José Elías of Analytical Department of ULL for the gas chromatographic measurements facilities. Beatriz González thanks the Gobierno Autónomo de Canarias for a predoctoral fellowship, and Éva Papp is grateful to the Hungarian Ministry of Education for a Békesy György postdoctoral scolarship.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2010.05.003.

References

[1] F. Joó, Aqueous Organometallic Catalysis, Kluwer, Dordrecht, 2001.
[2] B. Cornils, W.A. Herrmann (Eds.), Aqueous-Phase Organometallic Catalysis, 2nd ed., Wiley-VCH, Weinheim, 2004.
[3] D.J. Adams, P.J. Dyson, S.J. Tavener, Chemistry in Alternative Reaction Media, Wiley, Chichester, 2004.
[4] C.J. Li, Chem. Rev. 105 (2005) 3095–3165.
[5] S. Ahrland, J. Chatt, N.R. Davies, A.A. Williams, J. Chem. Soc. (1958) 276–288.
[6] F. Joó, J. Kovács, Á. Kathó, A.Cs. Bényei, T. Decuir, D.J. Darensbourg, Inorg. Synth. 32 (1998) 1–8.
[7] E. Kuntz, CHEMTECH 17 (1987) 570–575.
[8] W.A. Herrmann, C.W. Kohlpaintner, Inorg. Synth. 32 (1998) 8–25.
[9] D.J. Darensbourg, F. Joo, M. Kannisto, A. Katho, J.H. Reibenspies, Organometallics 11 (1992) 1990–1993.
[10] A.D. Phillips, L. Gonsalvi, A. Romerosa, F. Vizza, M. Peruzzini, Coord. Chem. Rev. 248 (2004) 955–993.
[11] B. Cornils, W.A. Herrmann, I.T. Horváth, W. Leitner, S. Mecking, H. Olivier-Bourbigou, D. Vogt (Eds.), Multiphase Homogeneous Catalysis, Wiley-VCH, Weinheim, 2005.
[12] F. Joó, Á. Kathó, in: J.G. de Vries, C.J. Elsevier (Eds.), Handbook of Homogeneous Hydrogenation, Wiley-VCH, Weinheim, 2007, pp. 1327–1359.
[13] K.H. Shaughnessy, Chem. Rev. 109 (2009) 643–710.
[14] M. Ito, S. Kitahara, T. Ikariya, J. Am. Chem. Soc. 127 (2005) 6172–6173.
[15] R.C. van der Drift, E. Bouwman, E. Drent, J. Organomet. Chem. 650 (2002) 1–24.
[16] R. Uma, C. Crévisy, R. Grée, Chem. Rev. 103 (2003) 27–52.
[17] V. Cadierno, P. Crochet, J. Gimeno, Synlett (2008) 1105–1124.
[18] A. Zoran, Y. Sasson, J. Blum, J. Org. Chem. 46 (1981) 255–260.

[19] B.M. Trost, R.J. Kulawiec, J. Am. Chem. Soc. 115 (1993) 2027–2036.
[20] J.-E. Bäckvall, U. Andreasson, Tetrahedron Lett. 34 (1993) 5459–5462.
[21] P. Crochet, M.A. Fernández-Zúmel, J. Gimeno, M. Scheele, Organometallics 25 (2006) 4846–4849.
[22] B. Martín-Matute, K. Bogár, M. Edin, F.B. Kaynak, J.-E. Bäckvall, Chem. Eur. J. 11 (2005) 5832–5842.
[23] C. Slugovc, E. Rüba, R. Schmid, K. Kirchner, Organometallics 18 (1999) 4230–4233.
[24] V. Cadierno, J. Francos, J. Gimeno, N. Nebra, Chem. Commun. (2007) 2536–2538.
[25] V. Cadierno, S.E. García-Garrido, J. Gimeno, Chem. Commun. (2004) 232–233.
[26] V. Cadierno, S.E. Garcia-Garrido, J. Gimeno, A. Varela-Álvarez, J.A. Sordo, J. Am. Chem. Soc. 128 (2006) 1360–1370.
[27] T. Campos-Malpartida, M. Fekete, F. Joó, Á. Kathó, A. Romerosa, M. Saoud, W. Wojtków, J. Organomet. Chem. 693 (2008) 468–474.
[28] V. Cadierno, P. Crochet, J. Francos, S.E. García-Garrido, J. Gimeno, N. Nebra, Green Chem. 11 (2009) 1992–2000.
[29] B. Lastra-Barreira, J. Díez, P. Crochet, Green Chem. 11 (2009) 1681–1686.
[30] P. Csabai, F. Joó, Organometallics 23 (2004) 5640–5643.
[31] M. Fekete, F. Joó, Catal. Commun. 7 (2006) 783–786.
[32] S.S. Bosquain, A. Dorcier, P.J. Dyson, M. Erlandsson, L. Gonsalvi, G. Laurenczy, M. Peruzzini, Appl. Organomet. Chem. 21 (2007) 947–951.
[33] P. Smoleński, F.P. Pruchnik, Z. Ciunik, T. Lis, Inorg. Chem. 42 (2003) 3318–3322.
[34] D.J. Darensbourg, F. Joó, M. Kannisto, Á. Kathó, J.H. Reibenspies, D.J. Daigle, Inorg. Chem. 33 (1994) 200–208.
[35] C.S. Allardyce, P.J. Dyson, D.J. Ellis, S.L. Heath, Chem. Commun. (2001) 1396–1397.
[36] C. Scolaro, A. Bergamo, L. Brescacin, R. Delfino, M. Cocchietto, G. Laurenczy, T.J. Geldbach, G. Sava, J. Paul, Dyson, J. Med. Chem. 48 (2005) 4161–4171.
[37] B. González, P. Lorenzo-Luis, P. Gili, A. Romerosa, M. Serrano-Ruiz, J. Organomet. Chem. 694 (2009) 2029–2036.
[38] E.M. Peña-Méndez, B. Gonzalez, P. Lorenzo, A. Romerosa, J. Havel, Rapid Commun. Mass Spectrom. 23 (2009) 3831–3836.
[39] D.J. Daigle, Inorg. Synth 32 (1998) 40–45.
[40] A. Romerosa, T. Campos-Malpartida, C. Lidrissi, M. Saoud, M. Serrano-Ruiz, M. Peruzzini, J.A. Garrido-Cárdenas, F. García-Maroto, Inorg. Chem. 45 (2006) 1289–1298.
[41] C.A. Mebi, R.P. Nair, B.J. Frost, Organometallics 26 (2007) 429–438.
[42] C. Scolaro, C.G. Hartinger, C.S. Allardyce, B.K. Keppler, P.J. Dyson, J. Inorg. Biochem. 102 (2008) 1743–1748.
[43] K.J. Powell, P.L. Brown, R.H. Byrne, T. Gajda, G. Hefter, S. Sjöberg, H. Wanner, Pure Appl. Chem. 77 (2005) 739–800.
[44] R.N. Goldberg, N. Kishore, R.M. Lennen, J. Phys. Chem. Ref. Data 31 (2002) 232–371.
[45] A. Romerosa, M. Saoud, T. Campos-Malpartida, C. Lidrissi, M. Serrano-Ruiz, M. Peruzzini, J.A. Garrido-Cárdenas, F. García-Maroto, Eur. J. Inorg. Chem. (2007) 2803–2812.
[46] M.S. Davies, S.J. Berners-Price, T.W. Hambley, Inorg. Chem. 39 (2000) 5603–5613.