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Mechanism of -O–O- bond activation and catalysis by Ru^{III}-pac complexes (pac = polyaminocarboxylate)

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Abstract. This paper presents the mechanistic aspects of the -O–O- bond activation by the Ru-pac (pac = polyaminocarboxylate) complex leading to the formation of various catalytic active species, viz. $[Ru^{III}(pac)(OOH)]^{2-}$, $[Ru^{IV}(pac)(OH)]^{-}$ and $[Ru^{V}(pac)(O)]^{-}$, and their reactivity towards oxidation of a few organic compounds.

Keywords. Kinetics; catalysis; -O–O- bond activation; Ru-pac complex; oxidation.

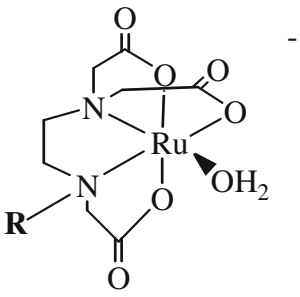
1. Introduction

Ru-pac complexes exhibit catalytic properties,[1] in homogeneous conditions in the presence of oxygen atom donors, that mimic the biological enzymatic oxidation of hydrocarbons by cytochrome P-450.[2,3] The natural P-450 enzymes when treated with an oxygen atom transfer agent such as H_2O_2 in the presence of large excess of a suitable substrate inside the hydrophobic site of the enzyme, it triggers the oxygen activation cycle and the releases oxygenated substrate, a hydrophilic molecule. Recently, mechanistic aspects of the reactions of $[Ru^{III}(edta)(H_2O)]^{-}$ with different oxidants, and its catalytic ability towards oxidation of some selected compounds of biological importance have been reviewed.[4] In this report, we briefly discuss the reactivity of $[Ru^{III}(pac)(H_2O)]$ complex in general towards O–O bond activation, and for this purpose results of some unpublished works on another ruthenium complex, $[Ru^{III}(hedtra)(H_2O)]$ (hedtra = N-hydroxyethylethylenediaminetriacetate), structurally similar (figure 1), but comparatively less labile than Ru-edta complex towards substitution reaction,[1] have been included. The present paper emphasizes the substitution behaviour of Ru-pac (pac = $edta^{4-}$, $hedtra^{3-}$) complexes which governs the efficiency of the catalysis of -O–O- activation.

2. Materials

$K[Ru^{III}(hedta)Cl].2H_2O$ was prepared by following the published procedure and characterized.[5] $K_2[RuCl_5(H_2O)]$ (1 mM) was reacted with Na_2H_2edta (1 mM) in $HClO_4$ (1 mM). The reaction mixture was refluxed for 2 h and the volume of the pale-yellow solution was then reduced until the complex began to precipitate from the solution. Addition of cold ethanol precipitated the pale-yellow product, which was filtered off and washed several times with a water–acetone (1:9) mixture until free of chloride, and finally dried under vacuum. Anal. Calculated for $K[Ru^{III}(Hedta)Cl].2H_2O$: C 24.0, H 3.42, N 5.59%; Found. C 23.8, H 3.45, N 5.63%. IR, ν/cm^{-1}: 1720 (free -COOH), 1650 (coordinated $-COO^{-}$). UV-VIS in H_2O: λ_{max}/nm ($\varepsilon_{max}/M^{-1}\,cm^{-1}$): 283 (2800 ± 50), 350 sh (680 ± 10). The micro-analysis and spectral data are in good agreement with that reported in the literature.[5] The pK_a values related to the acid-dissociation equilibria of the pendant carboxylic acid arm and the coordinated water molecules are 2.4 and 7.6, respectively, at 25°C.[6,7]

$K[Ru^{III}(hedtra)Cl]$ was prepared by following the published procedure.[8] The micro-analysis and spectral data are in good agreement with those reported in the literature.[8] Anal. Calculated for $C_{10}H_{15}N_2ClO_7KRu$: C, 26.6; H, 3.4; N, 6.2. Found: C, 26.5; H, 3.2; N, 6.1%. IR, ν/cm^{-1}: 1637 (coordinated $-COO^{-}$). UV-Vis in H_2O: λ_{max}/nm ($\varepsilon_{max}/M^{-1}\,cm^{-1}$): 285 (1250 ± 12). the $K[Ru^{III}(hedtra)Cl]$ complex rapidly converts into the $[Ru^{III}(hedtra)(H_2O]$ complex when dissolved in water.[8] The pK_a values related to the proton-dissociation equilibrium of the coordinated water molecule is 4.9 at 25°C.[8] All other chemicals used were of A.R grade. Doubly distilled H_2O was used throughout the experiments.



R = -COO⁻; pac = edta⁴⁻
R = -CH₂CH₂OH; pac = hedtra³⁻

Figure 1. Pictorial representation of $[Ru^{III}(pac)(H_2O)]$.

A Perkin Elmer 240C elemental analyzer was used to collect microanalytical (C, H, N) data. The UV-vis spectra were recorded on a Varian (Model Cary 100 Bio) spectrophotometer. A Perkin Elmer FT-IR spectrometer (Spectrum-65) was used for obtaining IR spectra (using KBr pellets). The kinetics of the reactions was followed spectrophotometrically by adopting a conventional mixing technique using the Varian Model Cary 100 Bio spectrophotometer. A tandem cuvette was used for this purpose.

3. Results and discussion

The 'pac' ligands function as pentadentate ligands (represented in figure 1) towards ruthenium, and the lability of such complexes is governed by the nature of the pendant group (R). The high lability is induced by the pendant group when $R = CH_2COO^-$, with significantly decreased lability for $R = CH_2CH_2OH$.[8] Notably, electrochemical studies of $[Ru^{III}(pac)(H_2O)]$ complexes have shown that the electron transfer process is rapid and reversible for the $[Ru^{III}(pac)(H_2O)]/[Ru^{II}(pac)(H_2O)]$ couple. The redox potential corresponding to $[Ru^{III}(pac)(H_2O)]/[Ru^{II}(pac)(H_2O)]$ couple for $[Ru^{III}(edta)(H_2O)]^-$ ($R = CH_2COO^-$) and $[Ru^{III}(hedtra)(H_2O)]$ ($R = CH_2CH_2OH$) complexes are −0.04 and −0.07 V (vs. NHE), respectively.[1] In view of the above electrochemical data, it appears that $[Ru^{III}(edta)(H_2O)]^-$ should be more oxidizing (by 30 mV) than $[Ru^{III}(hedtra)(H_2O)]$.

3.1 *Reaction of $[Ru^{III}(pac)(H_2O)]$ complex with oxygen atom donors*

Like $[Ru^{III}(edta)(H_2O)]^-$ complex, the reaction of $[Ru^{III}(hedtra)(H_2O)]$ complex with various oxygen atom donors, viz. ROOH = H_2O_2, *t*-BuOOH and HSO_5^- resulted in the formation of $[Ru^{V}(hedtra)(O)]$ complex.[9] Reaction of $[Ru^{III}(hedtra)(H_2O)]$ with ROOH exhibited a similar kinetic behaviour, but considerably slower reaction rate was observed than that of Ru-edta complex.[10,11] Spectral changes that were observed upon addition of ROOH to an aqueous solution of $[Ru^{III}(hedtra)(H_2O)]$ is typically shown in figure 2. In all cases the reaction was found to consist of two steps which involve the rapid formation of a $[Ru^{III}(hedtra)(OOR)]^-$ intermediate, followed by heterolytic cleavage of -O–O- bond to form $[(Ru^{V}(hedtra)(O)]$. Based on the above experimental observations, and considering the kinetic results reported earlier for the reaction of Ru-edta with ROOH,[10,11] a following mechanism for the activation of -O–O- bond in ROOH by Ru-pac complexes is proposed in scheme 1. Since $[Ru^{V}(pac)(O)]^-$ was produced predominantly in all cases, the common mechanism is one of heterolytic scission of the O–O bond (Eq. 2 in scheme 1). The values of the overall second-order rate constants, expressed as kK, i.e., the product of the equilibrium constant K for the formation of $[Ru^{III}(pac)(OOR)]^-$ and the rate constant k_1 for the subsequent heterolytic cleavage of the O–O bond to form $[Ru^{V}(pac)(O)]^-$, are 26.5, 1.45 and 7.0 $M^{-1}\,s^{-1}$ for ROOH = H_2O_2, ^{t}BuOOH and $KHSO_5$, respectively, at 25°C when pac = edta[4–10,11] For pac = hedtra^{3-}, the values are 8.2, 0.08 and 0.68 $M^{-1}s^{-1}$ for ROOH = H_2O_2, ^{t}BuOOH and $KHSO_5$, respectively, at 25°C. Since the overall reaction is a two-step process, the ability to form $[Ru^{III}(pac)(OOR)]$ (R = H, ^{t}Bu and HSO_3^-) species will predominantly govern the efficiency of O–O bond activation in the precursor oxidants, ROOH. The formation of

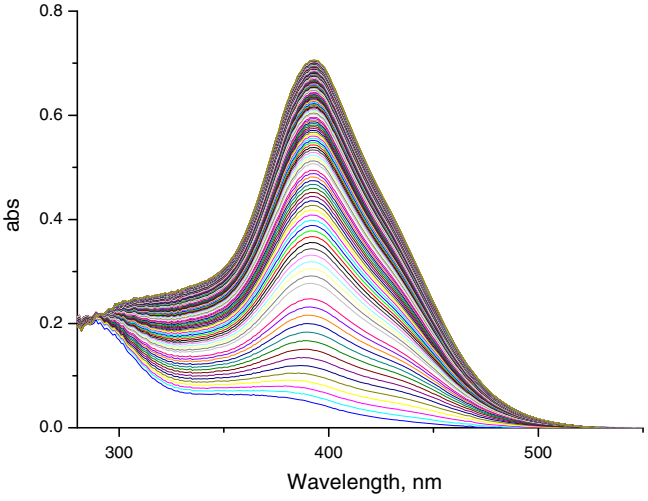


Figure 2. Spectral changes that occurred in the reaction of $[Ru^{III}(hedtra)(H_2O)]$ (1.0×10^{-4} M) and H_2O_2 (1×10^{-2} M) at pH 3.0 (1 mM acetate buffer).

$$[Ru^{III}(pac)(H_2O)] + H_2O_2 \underset{}{\overset{K}{\rightleftharpoons}} [Ru^{III}(pac)(OOH)]^- + H_3O^+ \quad (1)$$

$$[Ru^{III}(pac)(OOH)]^- \xrightarrow{k_1} [Ru^{V}(pac)(O)] + OH^- \quad (2)$$

$$[Ru^{III}(pac)(OOH)]^- \xrightarrow[H^+]{k_2} [Ru^{IV}(pac)(OH)]^- + OH\bullet \quad (3)$$

Scheme 1. Proposed reaction scheme for the reaction of $[Ru^{III}(pac)(H_2O)]$ with H_2O_2.

$[Ru^{III}(pac)(OOR)]$ species is governed by two factors: (i) nucleophilicity of ROOH and (ii) the lability of $[Ru^{III}(pac)(H_2O)]$ complexes towards aquo-substitution to from $[Ru^{III}(pac)(OOR)]$ intermediate complex in solution. It is noteworthy that the ability of the $[Ru^{III}(pac)(OOR)]$ intermediate complex to undergo heterolytic cleavage of the O–O bond expressed by the rate constant k_1, should correlate with the reduction potential of the different hydroperoxides under consideration, i.e., ^{t}BuOOH ($E^0 = 1.15$ V)[12] << H_2O_2 ($E^0 = 1.78$ V) ≤ HSO_5^- ($E^0 = 1.82$ V).[13] From a combination of the separate trends expected for k and K, and a comparison of the trend observed in the values of kK at 25°C, it follows that in addition to the electronic factors considered here, steric hindrance on ^{t}BuOOH and HSO_5^- as compared to H_2O_2 should further account for the fact that kK is significantly smaller for ^{t}BuOOH and HSO_5^- as compared to H_2O_2. The findings of this work taken together for the reaction of $[Ru^{III}(pac)(H_2O)]$ with H_2O_2, strongly suggest that the oxo-transfer from the precursor oxidant ROOH (H_2O_2, ^{t}BuOOH and $KHSO_5$) to $[Ru^{III}(pac)(H_2O)]$ that results in the formation of the $[Ru^{V}(pac)(O)]$ species should proceed through the formation of $[Ru^{III}(pac)(OOR)]$ intermediates (R = H, ^{t}Bu and SO_3^-) in a pre-equilibrium step, which subsequently undergoes rate-controlling heterolytic cleavage of the O–O bond to produce $[Ru^{V}(pac)(O)]$ as the major product (80–90%). However, in the reaction of $[Ru^{III}(pac)(H_2O)]$ with H_2O_2 leads to the rapid formation of the hydroperoxo species, $[Ru^{III}(pac)(OOH)]$, which subsequently undergoes heterolysis and homolysis of the O–O bond to form $[Ru^{V}(pac)(O)]$ and $[Ru^{IV}(pac)(OH)]$, respectively (see reactions 3 in scheme 1). The $[Ru^{IV}(edta)(OH)]^-$ complex did not show any characteristic band in the UV-Vis region,[14] whereas the $[Ru^{V}(pac)(O)]$ complex is characterized by a band at 390 nm.[9,15] Thus, the ^{t}Bu and SO_3^- substituents in $[Ru^{III}(pac)(OOR)]$ cause O–O bond cleavage to clearly favour heterolysis above homolysis. The above results demonstrate the capability to tune the fundamental nature of the O–O bond cleavage process, and underline the advantage of studying such Ru(III)-pac systems in such detail. The mechanistic information described above suggests that Ru-pac complexes could be promising species with regard to potential biological applications, especially in the elucidation of the mechanisms of reactive intermediates formed in enzymatic oxygenation reactions that could afford to understand the chemistry of *in vivo* processes in biological and bioinorganic chemistry. The considerably slower rate observed in case of Ru^{III}-hedtra complex as compared to its 'edta' analogue is consistent to the lesser lability of Ru^{III}-hedtra complex towards aquo-subsititution reported earlier,[8] for which formation of $[Ru^{III}(hedtra)(OOR)]$ species through aquo-substitution of $[Ru^{III}(hedtra)(H_2O)]$ with ROOH takes at slower rate than $[Ru^{III}(edta)(H_2O)]$ complex.

3.2 *Ru^{III}-pac catalysed oxidation of cysteine with H_2O_2*

Very recently we have reported Ru-edta catalysed oxidation of cysteine using H_2O_2 as oxidant.[16] Cysteine oxidation with cellular hydrogen peroxide is of biological significance *per se* with respect to oxidative stress and degenerative neurological disorder.[17,18] Furthermore, hydrogen peroxide acts as a key substance in various intracellular signalling pathways concerning protein phosphorylation through cysteine oxidation.[19] Recently, the possible role of $[Ru^{III}(edta)(H_2O)]^-$ in protein tyrosine phosphatase (PTP) inhibition of its biological activity has been explored.[20] $[Ru^{III}(pac)(H_2O)]^-$ reacts rapidly with cysteine (RSH) to form the S-coordinated red coloured $[Ru^{III}(pac)(SR)]^-$ complex.[21,22] However, rate of formation of $[Ru^{III}(edta)(SR)]^{2-}$ ($k = 170\ M^{-1}s^{-1}$ at 25°C)[21] is appreciably higher than that of $[Ru^{III}(hedtra)(SR)]^-$ ($k = 2.6\ M^{-1}s^{-1}$ at 25°C).[22] The red colour $[Ru^{III}(pac)(SR)]^-$ complex undergoes oxidation in the presence of H_2O_2 resulting in bleaching of the red colour which is attributed to the oxidation of the coordinated cysteine in $[Ru^{III}(pac)(SR)]^-$ under the specified conditions.[16] A mechanistic proposal in agreement

$$[Ru^{III}(pac)(H_2O)] + RSH \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [Ru^{III}(pac)(SR)]^- + H_3O^+ \quad (4)$$

$$[Ru^{III}(pac)(SR)]^- + H_2O_2 \xrightarrow{k^1_{ox}} [Ru^{III}(pac)(SROH)] + OH^- \quad (5)$$

$$[Ru^{III}(pac)(SROH)]^- + H_2O_2 \xrightarrow{k^2_{ox}} [Ru^{III}(pac)(H_2O)] + RSO_2H \quad (6)$$

$$[Ru^{III}(pac)(SROH)]^- + RSH \xrightarrow{k^3_{ox}} [Ru^{III}(pac)(H_2O)] + RSSR \quad (7)$$

Scheme 2. Mechanistic scheme for the Ru-pac catalysed oxidation of RSH with H_2O_2.

with the kinetic data and the product distribution profile for the Ru-edta catalysed oxidation of cysteine with H_2O_2 was already reported.[16] In the reported reaction scheme, attack of H_2O_2 to coordinated sulphur atom of cysteine in $[Ru^{III}(edta)(SR)]^{2-}$ was proposed to be the rate-determining step of the catalytic process.[16] A similar kinetic behaviour was observed for the reaction of H_2O_2 with thiolato complexes of ruthenium ($[Ru^{III}(hedtra)(SR)]^-$) but at an appreciably slower rate under trun-over conditions ([Ru]:[Cysteine]:$[H_2O_2]$ = 1:10:100). HPLC analysis for the oxidation products of the Ru-hedtra catalysed oxidation of cysteine with H_2O_2 also confirmed the formation of cysteine sulphinic acid (RSO_2H) and cystine (RSSR), as observed in case of cysteine oxidation catalysed by Ru-edta complex under specified conditions.[16] In view of the above, a general mechanism for Ru-pac complexes catalysed oxidation of cysteine with H_2O_2 is proposed in scheme 2. The $[Ru^{III}(pac)(SROH)]$ species so formed by the rate determining attack of H_2O_2 to the coordinated cysteine (Eq. 5) subsequently, reacts with H_2O_2 and RSH in reactions (6) and (7) to form RSO_2H (cysteine sulphinic acid) and RSSR (cystin), respectively as evidenced by the HPLC analyses of the reaction mixture. Both reactions (6) and (7) simultaneously regenerate $[Ru^{III}(pac)H_2O]$ that in turn reacts with free cysteine via reaction (4) to repeat the catalytic cycle. This step is very crucial in governing the efficiency of the catalytic process, and obviously Ru-edta is much more efficient catalyst due to its higher lability towards binding cysteine than its hedtra analogue. The formation of RSOH has been reported in the literature[23,24] and can undergo a rapid subsequent reaction with RSH to produce RSSR (cystin).[25] In the absence of $[Ru^{III}(pac)(H_2O)]$, RSH is only partially oxidized even after 900 s to form mainly RSSR along with trace amounts of RSO_2H as evidenced from HPLC analysis. Above results convincingly demonstrate the catalytic role of $[Ru^{III}(pac)(H_2O)]$ in the oxidation of cysteine by H_2O_2.

3.3 *Ru^{III}-pac catalysed oxidation of Orange II with H_2O_2*

Dyes, especially azo-dyes in waste-water are most harmful dye pollutants that create environmental problems.[26] Although safety and environmental concerns seems to have attached special importance to the use of hydrogen peroxide (H_2O_2) concerning dye degradation, azo-dyes are very difficult to oxidize and decompose with H_2O_2. In a very recent study, remarkable catalytic activity of the $[Ru^{III}(edta)(H_2O)]^-$ complex towards degradation of Orange II (ORII), a model azo dye in the presence of H_2O_2 has been reported.[27] Role of the hydroperoxo complex $[Ru^{III}(edta)(OOH)]^{2-}$ as the sole catalytic species for the degradation of ORII by hydrogen peroxide has been highlighted.[27] Furthermore, other intermediate species viz. $[Ru^{IV}(edta)(OH)]^-$ and $[Ru^{V}(edta)(O)]^-$ formed in the reaction of $[Ru^{III}(edta)(H_2O)]^-$ with H_2O_2 were

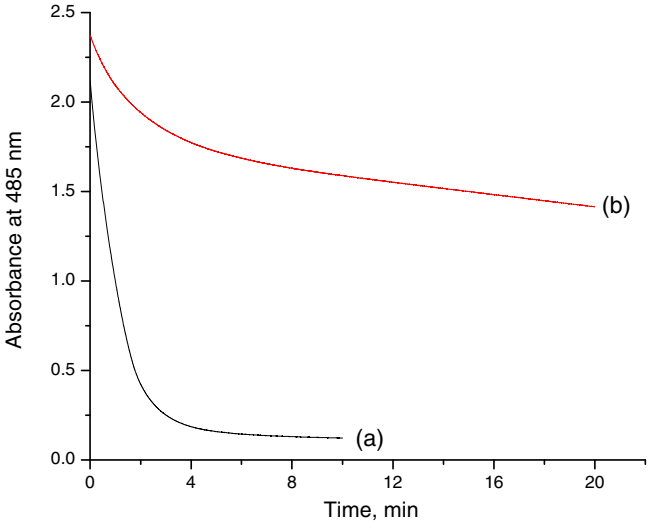


Figure 3. Degradation of ORII by (a) $[Ru^{III}(edta)(H_2O)]/H_2O_2$ and (b) $[Ru^{III}(hedtra)(H_2O)]/H_2O_2$ followed at 485 nm. $[Ru^{III}] = (5.0 \times 10^{-5}\,M)$, $[ORII] = (1 \times 10^{-4}\,M)$ and H_2O_2 $(1 \times 10^{-2}\,M)$ at pH 3.0 (1 mM acetate buffer).

$$[Ru^{III}(pac)(H_2O)] + H_2O_2 \underset{k'_r}{\overset{k'_f}{\rightleftharpoons}} [Ru^{III}(pac)(OOH)]^- + H_3O^+ \quad (8)$$

$$[Ru^{III}(pac)(OOH)] + ORII \xrightarrow{k^4_{ox}} [Ru^{III}(pac)(H_2O)] + \boxed{\text{Oxidation products of ORII}} \quad (9)$$

Scheme 3. Mechanistic scheme for the Ru-pac catalysed oxidation of ORII with H_2O_2.

shown to be considerably less reactive (at least by three orders of magnitude) than $[Ru^{III}(edta)(OOH)]^{2-}$ species towards degradation of ORII. Above kinetic observation has been further substantiated by the results of the studies of ORII degradation catalysed by Ru^{III}-hedtra/H_2O_2 system. Although a similar kinetic behaviour was noticed, much slower rate of degradation of ORII (figure 3) catalysed by Ru-hedtra was found as compared to ORII degradation by Ru-edta/H_2O_2 system.[27] A working mechanism is proposed (scheme 3) for the Ru-pac catalysed degradation ORII in the presence of H_2O_2. Above results signify the remarkably high activity of $[Ru^{III}(pac)(OOH)]^-$, the Ru equivalent of compound **0**, as compared to $[Ru^{IV}(pac)(OH)]$ and $[Ru^{V}(pac)(O)]$, the Ru equivalents of compounds **II** and **I**, respectively, towards the degradation of ORII. Therefore, $[Ru^{III}(pac)(OOH)]^-$ complex can apparently initiate the degradation of ORII via the pathway suggested for oxygen atom transfer by compound **0** in P450 type oxidation processes. Higher catalytic activity of Ru-edta complex could be explicable in terms of its high lability towards formation of $[Ru^{III}(edta)(OOH)]^{2-}$ via aquo-substitution of $[Ru^{III}(edta)(H_2O)]^-$ with H_2O_2. Apart from this, dangling acetate arm (figure 1) will also allow the intramolecular stabilization of the hydroperoxo intermediate species and lead to an increase in the catalytic activity of the complex.[27]

4. Conclusions

In this study the mechanistic aspects of the -O–O- bond activation and reactivity of various active species, viz. $[Ru^{III}(pac)(OOH)]^-$, $[Ru^{IV}(pac)(OH)]$ and $[Ru^{V}(pac)(O)]$ have been established. The Ru(III)-pac complex capable of catalyse the oxidation of cysteine using H_2O_2 as oxidant under ambient conditions, thus models the action of cysteine peroxidase. In this catalytic process, H_2O_2 directly attacks the coordinated cysteine to produce cysteine sulphenic acid (RSOH), which subsequently rapidly reacts with H_2O_2 and RSH to form RSO_2H and RSSR, respectively. For ORII oxidation, the $[Ru^{III}(pac)(OOH)]^-$ complex formed in the reaction of $[Ru^{III}(pac)(H_2O)]$ and H_2O_2, demonstrates that the ruthenium equivalent of compound **0** which is many orders more efficient than the equivalent complexes for compounds **I** and **II**, viz. $[Ru^{IV}(pac)(OH)]$ and $[Ru^{V}(pac)(O)]$, respectively.

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