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# Ruthenium(III) Catalyzed Oxidation of Hypoxanthine and Xanthine by Mn(VII) in Aqueous Brønsted Acid Solutions: A Kinetic and Mechanistic Study

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Mn(VII) is broadly utilized as an oxidizing specialist, however it couldn't oxidize hypoxanthine (HXAN) and xanthine (XAN) even in concentrated Brønsted acidic ($HClO_4$, $H_2SO_4$) media and at raised temperatures. In any case, the responses went through flawlessly in presence of millimolar arrangements of ruthenium chloride (Ru(III) or $RuCl_3$) in presence of fluid Brønsted acidic arrangements. Under synergist conditions, response complied with first request energy in [(Mn(VII)] and [Alkaloid] at steady causticity and temperature. Increase in [Ru(III)] dramatically sped up the reactions with a first order dependence on [catalyst] at constant acidity and temperature. The rate of oxidation was enhanced by an increase in the concentration of Brønsted acid ($HClO_4$, $H_2SO_4$). The rate increases observed were examined using the acidity function criteria of Zucker-Hammett, Bunnett and Bunnett-Olsen. The most logical mechanism, involving the involvement of the water molecule in the slow step, has been proposed based on observed Bunnett-Olsen criteria of acidity functions (as proton transferring agent).

**Keywords: Mn(VII) oxidation, Xanthine, Hypoxanthine, Ru(III) catalysis, Brønsted acid media.**

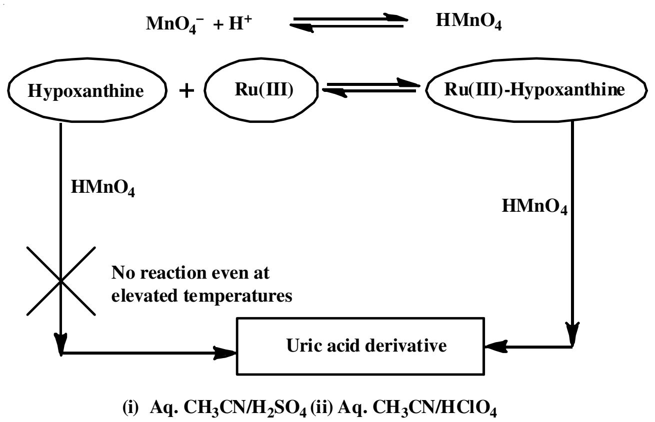
## INTRODUCTION

Potassium permanganate ($KMnO_4$) is a well-known powerful oxidizing agent, which can oxidize a wide range of organic compounds in acidic and alkaline solutions, which can oxidize a wide range of organic molecules. Oxidation studies with this compound are attractive environmental remedies due to its low cost, greater ease of use and wide range of reactivity [1-3]. Over the years, it has been used for selective oxidation of a broad spectrum of electron rich organic functional compounds like phenols, olefins, amino acids, thiols, ethers, carbonyl compounds [4-9]. Hypoxanthine is a purine group alkaloid, which has an immense biological importance and used as a necessary additive in certain cell, bacteria and parasite cultures, where in it acts as a substrate and nitrogen source [10]. Literature revealed that an oxidation of hypoxanthine forms xanthine is an intermediate, which upon degradation gives uric acid [11].

In a recent article, we looked at the Mn (VII) oxidation of caffeine, theophylline, and theobromine in aqueous acetonitrile and sodium fluoride with Bronsted acid as a catalyst [4]. However, hypoxanthine (HXAN) and xanthine (XAN) from the purine group of alkaloids were not oxidised by Mn(VII) even in concentrated Brønsted acid ($HClO_4$, $H_2SO_4$) media and at high temperatures. However, the reactions underwent smoothly in presence of millimolar solutions of silver nitrate or Ru(III)in presence of aqueous Brønsted acid solutions. Stimulated by the preliminary observations, we have taken up a detailed kinetic study oxidation of hypoxanthine and xanthine by Mn(VII) using catalytic amounts (millimolar solutions) of Ru(III) in aqueous Brønsted acid solutions (**Scheme-I**).

## EXPERIMENTAL

Analytical-grade chemicals were employed throughout. When necessary, doubly distilled water was employed (distilled over alkaline $KMnO_4$ and acid dichromate in an all glass system). The work was conducted with HPLC grade acetonitrile and other solvents. $Ru(NO_3)_3$, $KMnO_4$ and hypoxanthine (HXAN) and xanthine (XAN) were acquired from Aldrich, E-Merck, or S.D. fine chemicals.



**Scheme-I:** Ru(III) catalyzed Mn(VII) oxidation of xanthine and hypoxanthine

**Stoichiometry and products of oxidation:** In a typical experiment, 50 mL of aqueous acid medium containing xanthine alkaloid (0.01 mol substrate), Mn(VII) (0.015 mol) and millimolar Ru(III) were prepared and allowed to react until the reaction was complete. Periodically, the absorbance of Mn(VII) was measured and found that 1 mol of Mn(VII) was required to oxidize 1 mol of xanthine alkaloid substrate based on the change in absorbance values of Mn(VII). Following the completion, dichloromethane (2 × 25 mL) was used to extract the contents of the reaction mixture and then cleaned with water (40 mL). Over $MgSO_4$, a layer of dichloromethane (DCM) was separated and dried. The final product was obtained by purifying the residue using flash column chromatography ($SiO_2$, ethyl acetate-hexane, 1:2) after the solvent had evaporated. Identified by IR, NMR and mass analyses as a derivative of uric acid.

**Kinetic studies:** The flask was clamped in a thermostatic (constant temperature) bath and contained known quantities of substrate (xanthine/hypoxanthine), Brønsted acid ($HClO_4$/$H_2SO_4$), Ru(III) catalyst and an appropriate amount of solvent (aqueous acetonitrile). Another flask, which was likewise clamped in same thermostatic bath, contained $KMnO_4$ solution ($Mn^{7+}$). After reaching the thermal equilibrium, the reaction was started by quickly and completely mixing the necessary amount of Mn(VII) with the other contents of the reaction vessel. Flask has a black outside coating to shield it from the photochemical reactions. A reaction mixture was taken in aliquots, placed in a cuvette and then placed in the cell compartment of a visible spectrophotometer. An inlet and an exit were included in the cell compartment to allow thermostatic liquid to circulate at the required temperature. The previously created calibration curve, which displays absorbance *versus* [Mn(VII)], might be used to estimate the Mn(VII) concentration. With an accuracy of ± 3% inaccuracy, absorbance measurements agreed with one another.

**Determination of order of reaction:** The first order rate equation under hypothetical conditions was employed to determine the order of reaction utilizing the graphical technique of approach [12-15] [Substrate] >> [Mn(VII)]:

$$\ln\left(\frac{A_0}{A_t}\right) = (k')t \quad (1)$$

where $A_0$ and $A_t$ are the absorbance values at zero time (when the reaction began) and at a certain point in time (during the reaction's progression), respectively. Additionally, although $A_t$ is proportional to the concentration of Mn(VII) at a specific time "t", while $A_0$ is proportional to the initial concentration of $KMnO_4$ ($[Mn(VII)]_0$). Inferring first order kinetics in [Mn(VII)], the plots of $[\ln(A_0/A_t)]$ *vs.* time were linear passing through the origin (figures not shown). Additionally, under second order conditions, the equimolar solutions of Mn(VII) and xanthene alkaloid (substrate) were added to the reaction mixture (*i.e.* when $[Mn(VII)]_0 = [Substrate]_0$) and the plots of $[1/(A_t)]$ *vs.* time were found to be linear with a positive gradient and definite intercept on the vertical axis, indicating overall second order kinetics, according to the following expression:

$$\frac{1}{A_t} = \frac{k}{(\varepsilon)}t + \frac{1}{A_0} \quad (2)$$

where, $\varepsilon = [Mn(VII)]_0/(A_0)$.

Substituting $([Mn(VII)]/A_0)$ for ($\varepsilon$), the above equation becomes:

$$\frac{1}{A_t} = \frac{k[Mn(VII)]_o}{(A_0)}t + \frac{1}{A_0} \quad (3)$$

The aforementioned findings showed that reaction kinetics at constant acidity follow a general second order and since the linearity of $[\ln(A_0/A_t)]$ *vs.* time indicates that [Mn(VII)] has a first order, it follows that the order in [Substrate] is also one. As a result, the ratio of the observed slope to intercept on the second order plot ($k = \text{slope/intercept} * [Mn(VII)]_0$) can be used to determine the second order rate constant (k). However, in the current work, the slopes of k′ *versus* [Substrate] were used to determine the second order rate constant (k).

**Activation parameters:** In the temperature range of 300-325 K, various kinetic parameters have been evaluated. Following the well-known theory of reaction rates [12-15], the free energy of activation ($\Delta G^\#$) at various temperatures is computed using Eyring's equation.

$$\Delta G^\# = RT\ln\left(\frac{RT}{Nhk}\right) \quad (4)$$

Substituting the values for R (8.314 J/mol K), N ($6.022 \times 10^{23}$/mol), h ($6.626 \times 10^{-34}$ J s) and T (Kelvin degrees) respectively, $\Delta G^\#$ could be simplified accordingly as:

$$\Delta G^\# = 8.314 \times T\,[23.7641 + \ln(T/k)] \quad (5)$$

According to the Gibbs-Helmholtz equation [12-15], the enthalpy and entropies of activation ($\Delta H^\#$ and $\Delta S^\#$) were calculated from the plot of $\Delta G^\#$ *vs.* temperature (T):

$$\Delta G^\# = \Delta H^\# - T\Delta S^\# \quad (6)$$

## RESULTS AND DISCUSSION

In present study, variation of [acid] accelerated the reaction rate (Table-1). A review of literature reveals that in aqueous acid media, $KMnO_4$ is known to exist as permanganate anion ($MnO_4^-$) and permanganic acid ($HMnO_4$) due to the protonation of permanganate anion [6,7] according to the following protonation equilibrium:

TABLE-1
EFFECT OF VARIATION OF [ACID] IN Ru(III) CATALYZED Mn(VII) OXIDATION OF ALKALOIDS

| [Acid] (mol/dm$^3$) | (k′/min) in $H_2SO_4$ medium | | (k′/min) in $HClO_4$ medium | |
|---|---|---|---|---|
| | XAN | HXAN | XAN | HXAN |
| 0.40 | 1.2625 | 1.200 | 1.2875 | 1.4375 |
| 0.80 | 1.3500 | 1.275 | 1.4250 | 1.5750 |
| 1.20 | 1.4125 | 1.350 | 1.5250 | 1.6750 |
| 1.60 | 1.4875 | 1.500 | 1.6625 | 1.7875 |
| 2.00 | 1.5625 | 1.600 | 1.8250 | 1.9250 |

$$H^+ + MnO_4^- \overset{K}{\rightleftharpoons} HMnO_4$$

(K = 2.99 × $10^{-3}$ dm$^3$/mol at 25 ºC).

However, neither hypoxanthine nor xanthine underwent the reaction, even in extremely acidic solutions. However, in the presence of Ru(III), reactions proceeded smoothly. The reaction rate rose as [Ru(III)] increased and the plot of k′ *versus* [Ru(III)] was found to be linear, confirming that no uncatalyzed reactions occurred. However, Pullin & Pollock [16] established that Ru(III) forms colourless complexes with compounds containing oxygen when the oxygen atom has a single pair of electrons.

The rate dependence on acidity can be understood in moderate acidic medium (acidity ≥ 0.100 mol/dm$^3$) by using one of several acidity models developed by Zucker-Hamett, Bunnett and Bunnett-Olson [17-24]. The observed rate accelerations in different Brønsted acid concentrations were characterized by Zucker-Hamett (log (k) *vs.* ($H_0$); log (k) *vs.* log [Acid]), Bunnett ([log (k + ($H_0$)] *vs.* log ($a_w$); [log (k) – log (acid)] *vs.* log ($a_w$) and Bunnett-Olson [(log k + $H_0$) *vs.* ($H_0$ + log [$H^+$]]; (log k) *vs.* ($H_0$ + log [$H^+$]) plots were linear, with characteristic slopes, showing good to excellent correlation coefficients (0.995 > $R^2$ > 0.980). Table-2 lists the observed slopes of the plots used in this investigation by Zucker-Hamett (m and m$^\#$), Bunnett (ω and ω$^\#$) and Bunnett-Olsen (ϕ, or ϕ$^*$). These slopes are useful in indicating the role of the water molecule and its importance in the rate-determining stage of the mechanism. Table-2 clearly shows that all substrates have linear Zucker-Hammett plots of log (k) *vs.* ($H_v$) and log (k) *vs.* log [Acid], but none of them showed ideal unit slopes, indicating that water molecules were involved in the rate-determining phase. At the same time, Bunnett's slopes gave unassumingly high slopes. However, the Bunnett-Olsen's slopes are somewhat in the range of suggesting water molecule participation either as a nucleophile or as a proton transfer reagent in the slow step as reported earlier [6,7].

Based on the aforementioned kinetic characteristics, the most likely mechanism might be described as the first-step establishment of [Ru(III)-Mn(VII)], which then reacts with alkaloid in the slow step to produce products as indicated in **Scheme-II**.

At constant acidity, the rate-law for the above scheme could be derived by considering the total concentration of ($C_{Mn(VII)}$) as the algebraic sum of free Mn(VII) species and Ru(III) bound Mn(VII) species ([Ru(III)-Mn(VII)]) species. By taking the overall concentration of ($C_{Mn}$(VII)) as the algebraic sum of free Mn(VII) species and Ru(III) bound Mn(VII) species ([Ru(III)-Mn(VII)] species, the rate-law for the above scheme could be determined at constant acidity.

$$CMn(VII) = [Mn(VII)] + [Ru(III)\text{-}Mn(VII)] \quad (7)$$

From the Micelle-Mn(VII) binding equilibrium:

$$K_M = [Ru(III)\text{-}Mn(VII)]/[Ru(III)]\,[Mn(VII)] \text{ or}$$
$$[Mn(VII)] = [Ru(III)\text{-}Mn(VII)]/K_M\,[Ru(III)]$$

Substitution in eqn. 7 gives:

$$CMn(VII) = [Ru(III)\text{-}Mn(VII)] + [Ru(III)\text{-}Mn(VII)]/K_M\,[Ru(III)]$$

$$\rightarrow CMn(VII) = \{K_M\,[Ru(III)\text{-}Mn(VII)]\,[Ru(III)] + [Ru(III)\text{-}Mn(VII)]\}/K_M\,[Ru(III)]$$

$$\rightarrow CMn(VII) = [Ru(III)\text{-}Mn(VII)](1+ K_M\,[Ru(III)])/K_M\,[Ru(III)]$$

$$\rightarrow [Ru(III)\text{-}Mn(VII)] = K_M\,[Ru(III)]\,CMn(VII)/(1+ K_M\,[Ru(III)]) \quad (8)$$

But rate of the reaction (V) at constant acidity is written as:

$$Rate\ (V) = k\,[S]\,[Ru(III)\text{-}Mn(VII)]$$

(where, S = xanthine or hypoxanthine) substituting for [Ru(III)-Mn(VII)], the rate law becomes:

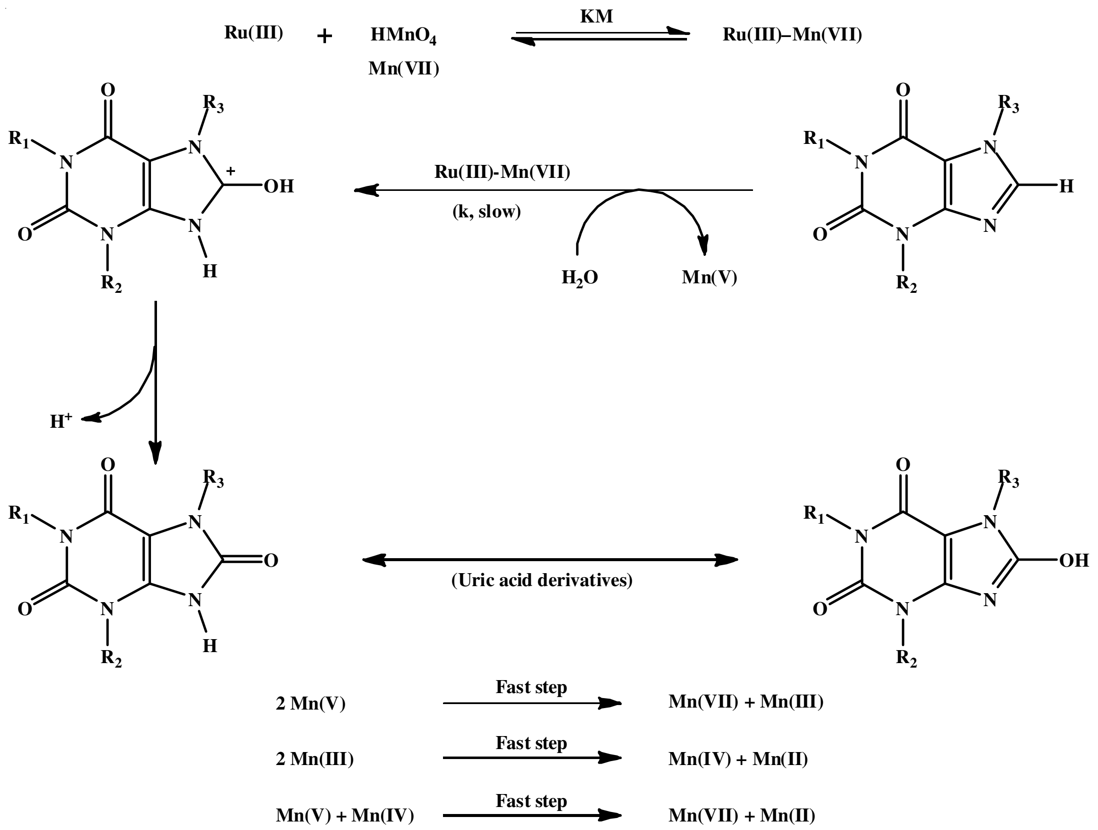
$$V = k\,K_M\,[S]\,[Ru(III)]\,CMn(VII)/(1+ K_M\,[Ru(III)]) \quad (9)$$

$$V/CMn(VII) = k' = k\,K_M\,[S]\,[Ru(III)]/(1+ K_M\,[Ru(III)]) \quad (10)$$

This rate-law is comparable to Menger-equation Portnoy's in micellar catalysis and the Michaelis-Menten type rate law

TABLE-2
ACIDITY FUNCTION PLOTS (XANTHINE DERIVATIVES) IN DIFFERENT ACID MEDIA

| Compound | Theory/Plot | Parameter | $H_2SO_4$ | | $HClO_4$ | |
|---|---|---|---|---|---|---|
| | | | Slope | $R^2$ | Slope | $R^2$ |
| Xanthine | Zucker-Hammett-I | M | 0.124 | 0.9683 | 0.2068 | 0.9493 |
| | Zucker-Hammett-II | m* | -0.0958 | 0.9874 | -0.1679 | 0.9941 |
| | Bunnett-III | ω | 12.984 | 0.9945 | -8.3713 | 0.9726 |
| | Bunnett-IV | ω* | -11.808 | 0.9683 | 9.8576 | 0.9831 |
| | Bunnett-Olsen-V | ϕ | -1.2949 | 0.922 | -1.1295 | 0.93 |
| | Bunnett-Olsen-VI | ϕ* | 1.242 | 0.9051 | 1.3278 | 0.9965 |
| Hypoxanthine | Zucker-Hammett-I | M | 0.1757 | 0.9538 | 0.1741 | 0.9653 |
| | Zucker-Hammett-II | M* | -0.1352 | 0.9825 | -0.14 | 0.9918 |
| | Bunnett-III | ω | 12.423 | 0.995 | -8.3713 | 0.9272 |
| | Bunnett-IV | ω* | -12.369 | 0.9768 | 10.18 | 0.9816 |
| | Bunnett-Olsen-V | ϕ | -1.2436 | 0.9294 | -1.1658 | 0.9275 |
| | Bunnett-Olsen-VI | ϕ* | 1.2933 | 0.9954 | 1.2921 | 0.9977 |



**Scheme-II:** Ru(III) catalyzed Mn(VII) oxidation of xanthine alkaloids

utilized in enzyme kinetics [25,26]. The Benesi-Hildebrand equation as applied to molecular/charge-transfer interactions [27-29] has been used to spectrophotometrically evaluate the binding constants ($K_M$) for Mn(VII) and Ru(III) micellar interactions. The results are shown in Table-3, which shows that the results on the binding constants ($K_M$) for sulfuric acid were slightly greater than those for perchloric acid. The binding constants in both the acid media somewhat decreased as the temperature increases from 303 K to 333 K.

TABLE-3
Mn(VII)–Ru(III) INTERACTIONS IN DIFFERENT ACIDIC MEDIA

| Medium | Temp. (K) | Binding constant ($K_M$) | ε (molar absorptivity) |
|---|---|---|---|
| $H_2SO_4$ | 303 | 8.6338 | 23.4742 |
| | 313 | 8.4614 | 22.0751 |
| | 323 | 7.7012 | 19.5313 |
| | 333 | 6.8818 | 16.8919 |
| $HClO_4$ | 303 | 4.6258 | 15.3374 |
| | 313 | 4.6157 | 14.8368 |
| | 323 | 4.4511 | 13.9665 |
| | 333 | 4.3641 | 13.1926 |

A further insight into rate eqn. 9: clearly depicts that the value of $K_M$[Ru(III)] << 1. There ($K_M$[Ru(III)]) could be neglected in the denominator. Accordingly, rate law reduces to second order rate law at constant acidity and [Ru(III)]. The rate constants ($k_m$) and corresponding activation parameters have been compiled in Table-3. An additional understanding of rate eqn. 9 makes it abundantly evident that the value of $K_M$[Ru(III)] << 1. It is possible to ignore $K_M$[Ru(III)] in the denominator. As a result, for constant acidity and [Ru(III)], rate law is reduced to second order rate law.

**Enthalpy and entropy changes:** The molecularity of the reaction's rate-determining step can be inferred from the entropy of activation ($\Delta S^{\#}$). Entropy values with positive values for $\Delta S^{\#}$ suggest that entropy increases after reaching the transition state, which frequently denotes a dissociative process, whereas values with negative values for $\Delta S^{\#}$ denote an associative mechanism [18-21]. Table-4 shows the negative $\Delta S^{\#}$ values, indicating that an associative process is at work in this study as a result of the interaction between Mn(VII) and Ru(III), which results in Ru(III)-bound Mn(VII).

## Conclusion

By using $KMnO_4$ in the catalytic concentrations, the oxidation of xanthine alkaloids such as xanthine (XAN) and hypoxanthine (HXAN) was carried out. Uric acid derivatives were gnerated by oxidizing the xanthine derivatives. Even at high temperatures, the reaction is too slow in the acetonitrile medium, but it proceeded without any problems in the presence of the micelle-forming Ru(III) surfactant. The first order kinetics were used in both [$KMnO_4$] and [xanthine alkaloid] reactions. As [Ru(III)] increases, the rate of oxidation linearly accelerates. The slow step reaction between substrate and Ru(III)-bound Mn(VII) could be used to explain the mechanism of oxidation. This argument may be supported by the negative activation entropy values found in the present investigation.

TABLE-4
TEMPERATURE DEPENDENT OF KINETIC AND ACTIVATION PARAMETERS

| Substrate | Temp. (K) | $(k_m)$ $(dm^3/mol/min)$ | $\Delta G^{\#}$ (kJ/mol) | GH equation | $\Delta H^{\#}$ (kJ/mol) | $-\Delta S^{\#}$ (J/K/mol) |
|---|---|---|---|---|---|---|
| (A) Sulfuric acid medium | | | | | | |
| Xanthine | 298 | 1.1125 | 72.7 | y = 0.2318x + 3.664 | 3.66 | 232 |
| | 313 | 1.2125 | 76.3 | | | |
| | 323 | 1.325 | 78.6 | | | |
| | 333 | 1.45 | 80.8 | | | |
| Hypoxanthine | 298 | 1.0625 | 72.8 | y = 0.217x + 8.2625 | 8.26 | 217 |
| | 313 | 1.2 | 76.3 | | | |
| | 323 | 1.425 | 78.4 | | | |
| | 333 | 1.675 | 80.4 | | | |
| (B) Perchloric acid medium | | | | | | |
| Xanthine | 298 | 2.275 | 70.9 | y = 0.222x + 4.7999 | 4.80 | 222 |
| | 313 | 2.6 | 74.3 | | | |
| | 323 | 2.825 | 76.5 | | | |
| | 333 | 3.125 | 78.7 | | | |
| Hypoxanthine | 298 | 2.65 | 70.6 | y = 0.2274x + 2.8192 | 2.82 | 227 |
| | 313 | 2.85 | 74.1 | | | |
| | 323 | 3.1 | 76.3 | | | |
| | 333 | 3.325 | 78.5 | | | |

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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