To Dr. Katalin Ősz
Associate professor
Department of General and Physical Chemistry, University of Pécs – Hungary
Answer to comments and suggestions on the PhD dissertation of

BASHDAR ISMAEL MEENA
entitled

IRON AND MANGANESE COMPLEXES IN BIOMIMETIC CATALYTIC OXIDATIONS

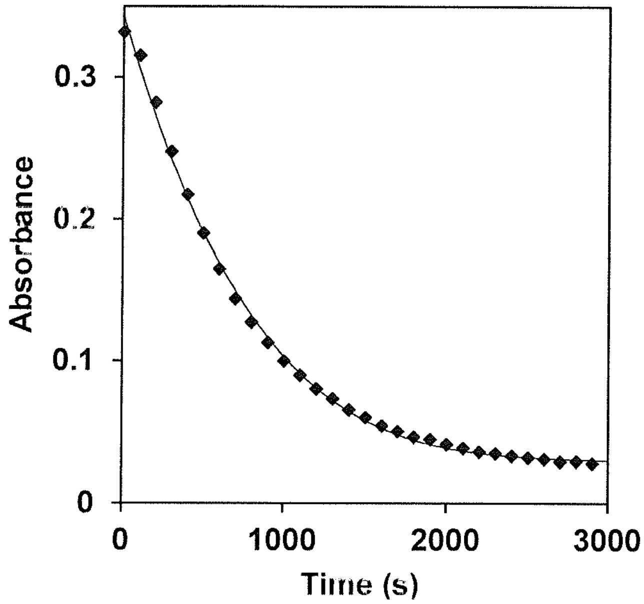
I am thankful to the worthy reviewer **associate professor Dr. Katalin Ősz**, for her valuable comments on my PhD theses and dissertation. I have answered the comments and suggestions of the reviewer in detail which helped me in producing a well-established final version of PhD theses and dissertation. Her comments were helpful in technical, academic and structural perspective. I appreciate her nice cooperation in providing a comprehensive review on my PhD theses and dissertation. After the submission of final hard copy to her, she has few more comments which are answered as given below.

Q1. The estimated errors for rate constants and other parameters with more details about the method used to calculate them?
Answer Q1: UV visible spectrophotometry was used in the measuring of all values of rate constants and the estimated error given by programme of the UV-visible.
Other parameters such as, activation energy, entropy and enthalpy were calculated from the correlation between k_2 and temperature dependent and estimated errors calculated by using the program developed by Prof. Gábor Lente.

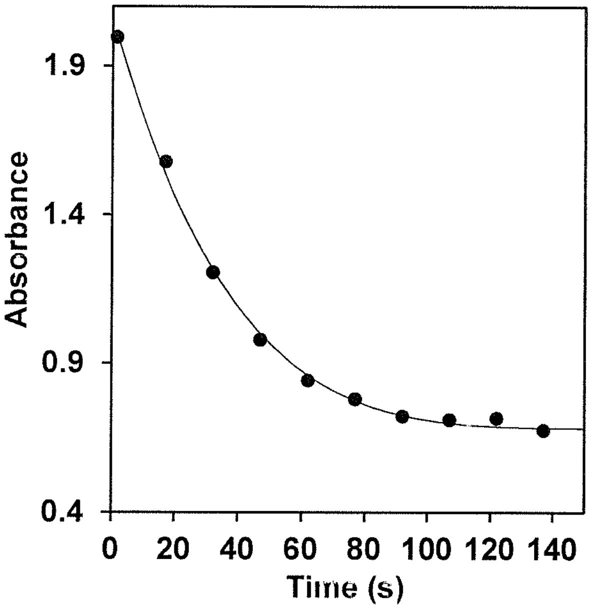
$E_A = 2.303 \times R \times d\log(k)/d\,(T^{-1})$
E_A Cycloocten = $2.303 \times 8.314 \times 2.113 = 41.41 \pm 3.16$ kJ×mol^{-1}
E_A Styrene = $2.303 \times 8.314 \times 3.801 = 72.7 \pm 1.23$ kJ×mol^{-1}
$\Delta H^{\neq} = 2.303\ R \times d\log(kT^{-1})/d\,(T^{-1})$
$\Delta H^{\neq}$ Cycloocten = $2.303 \times 8.314 \times 2.013 = 38.35 \pm 2.36$ kJ×mol^{-1}
$\Delta H^{\neq}$ Styrene = $2.303 \times 8.314 \times 3.71 = 71 \pm 3.3$ kJ×mol^{-1}

Q2. Kinetic trace curve for first-order of figures 11-12 and 28-30

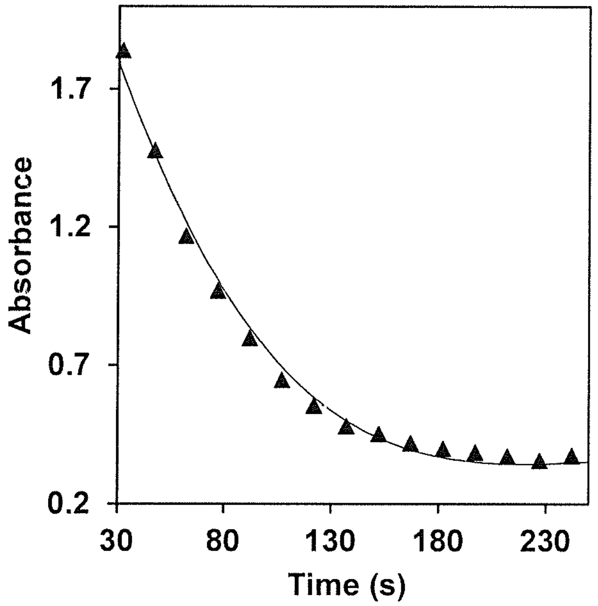
Answer Q2:



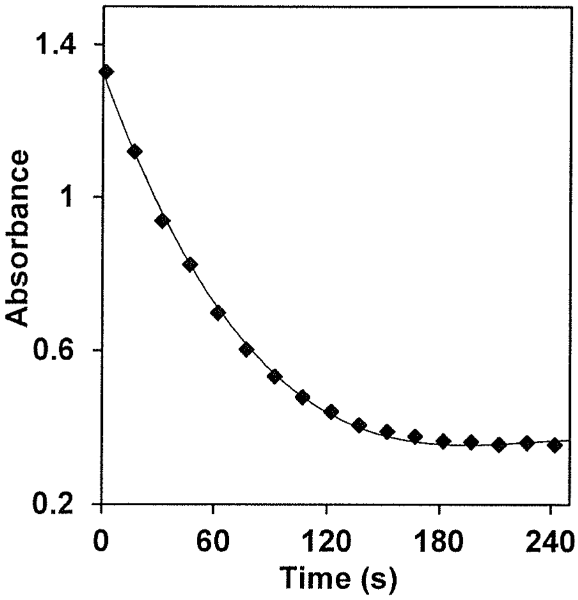
Kinetic trace curve in the reaction between $[Fe^{IV}(O)(asN4Py)]^{2+}$ and Cis cyclooctene at 705 nm



Kinetic trace curve for degradation of morin in the presence of hydrogen peroxide by Mn(II)



Kinetic trace curve for degradation of morin in the presence of Mn(II) complex



Kinetic trace curve for degradation of morin in the presence sodium bicarbonate by Mn(II) complex

Q3. Nonlinear least-squares fitting use to evaluate kinetic trace?

Answer Q3: Nonlinear least-squares is the best and effective method for fitting data of first-order kinetics [1, 2]. The initial rate determined from nonlinear least-square fitting (figure 1) was almost the same as the values calculated from formula $V = k_{obs}$ **[1b]**, because of k_{obs} independent of the concentration of complex. Based on that the linear correlation between rate reaction and complex concentration was established.

The linear plot of the reaction rate values $V = k_{obs}$ [**1b**] versus the initial concentration of (**1b**) (figure 2), states that the reaction is first-order with respect to the oxoiron(IV) concentration, results found a rate law of -d[**1b**]/dt = k_2[**1b**][alkene] for both substrates.

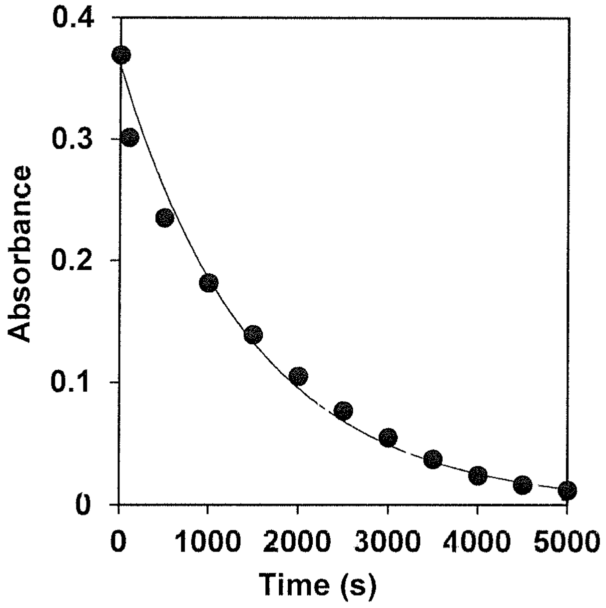


Figure 1. Nonlinear least-square fitting curve in the reaction between $[Fe^{IV}(O)(asN4Py)]^{2+}$ and styrene at 705 nm

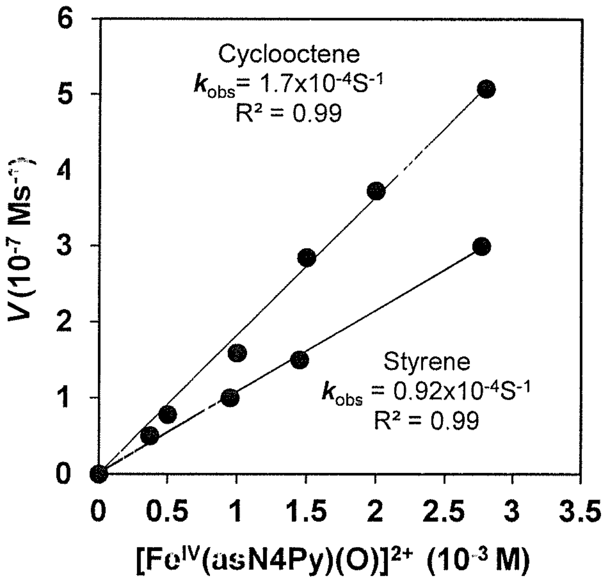
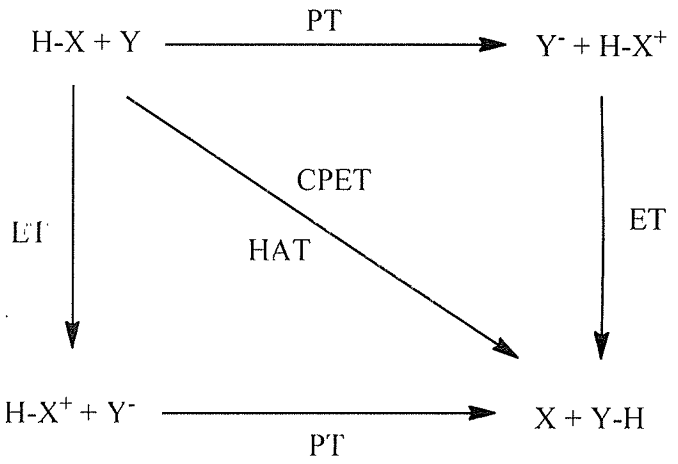


Figure 2. Plot of V versus $[Fe^{IV}(asN4Py)(O)]^{2+}$ 1.5×10^{-3} M, with for reactions of (0.3 M) cis-cyclooctene and styrene in CH_3CN at 298 K

Q4. Explain in details of the concepts proton-coupled electron transfer (PCET)?

Answer Q4; Proton-coupled electron transfer (PCET) is an abundant elementary process in chemistry [3], the essential properties of PCET systems can be considered by measuring the kinetic isotope effect (KIE) [4]. Recently, the concept of H^+/e- transfer processes have been presented by Meyer and Costentin [5], which is named as, proton-coupled electron transfer (PCET). It includes many redox processes where the rate or energetics are affected by one or more protons, involving processes in which protons and electrons transfer among one or more reactants by concerted. Also, Babcock and co-workers explained in details on the coupling of electron and proton transfer in Photosystem II and enzyme [6].

Hammarström and co-workers interpreted the one-step process for the term concerted electron/proton (CEP), which contrasts to stepwise processes involving either initial PT followed by ET, or ET followed by PT. The thermochemistry of the total PCET reaction is path-independent, therefore the free energy of the diagonal PCET reaction is equivalent to the sum of either ET/PT or PT/ET stepwise pathways around the edges of the square [7, 8], the scheme shows essential to understanding any PCET system.



Scheme Concerted vs. Stepwise Transfer of e^- + H^+ [8]

Q5. Correlation between TOF and potential in figures 39 and 50?

Answer Q6; Turnover number (TON) is the maximum number molecules of the substrate that can be converted into product per catalytic site of a given catalyst under defined conditions. Turnover frequency (TOF) is the measure of the specific activity of a catalytic centre of a given catalyst by the number of molecular reactions or catalytic cycles occurring at the centre per unit time [9]. According to Lente, G. published review paper, Kozuch and Martin tried to clarify TON and TOF concepts, which are commonly used in catalytic studies. Despite its utility and common use, the turnover frequency (TOF) concept is still not well-defined. The concept of TOF is focused on kinetic information about the catalytic reactions while, turnover number (TON) depicts stoichiometric information [10]. Another point Lente, G. mentioned in the reviewed paper, Kozuch and Martin correctly interpreted and compared TOF, However, he also has disagreement in some points with them such as, to full characterization and efficiency of catalyst should use rate law instead of turnover frequency (TOF) [10]. Bligaard and co-workers, reported that the term turnover number (TON) is still used to describe the activity turnover frequency (TOF) of enzymatic systems [11].

I agree with the reviewer, it is more favourable to establish the correlation between rate reaction and potential. However, in my case, I cannot follow the reactions to find the initial rate which is more accurate to calculate TOF value. Therefore, after finding the right conditions for the reaction such as, constant temperature and concentrate for the reactions, turnover frequency (TOF) was then calculated from the product formed.

Q6. Define Total substituent effect (TF) and gives a reference for it?

Answer Q6; **Total substituent effect (TF)**: It can be defined by the total effect of polar parameters and radical stabilization parameters of the substituent effect on carbon radical systems. The relative radical stabilities are mainly determined by the spin delocalization effect of the substituents [12, 13].

With best regards

PhD candidate
Bashdar Ismael meen

Date 5/11/2020

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