

Kinetics of photoinduced electron transfer reactions of ruthenium(II) complexes and phenols, tyrosine, *N*-acetyl-tyrosine and tryptophan in aqueous solutions measured with modulated fluorescence spectroscopy



Truong X. Nguyen^{a,b,*}, Stephan Landgraf^a, Günter Grampp^{a,*}

^a Institute of Physical and Theoretical Chemistry, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria

^b School of Chemical Engineering, Hanoi University of Technology, Dai Co Viet 1, Hanoi, Vietnam

ARTICLE INFO

Article history:

Received 24 August 2016

Accepted 5 November 2016

Available online 8 November 2016

Keywords:

Photoinduced electron transfer

Ruthenium(II) polypyridine complexes

Phenols

Tyrosine

N-acetyl-tyrosine

Tryptophan

Steric

Hydrophobic interaction

Phase-modulated fluorescence

ABSTRACT

Photooxidation kinetics of phenol, 1-naphthol, 2-naphthol, tyrosine (TyrOH) and *N*-acetyl-tyrosine (AcTyrOH), tryptophan (TrpH) by ruthenium(II) polypyridyl complexes: [Ru(bpy)₃]Cl₂ (**1**), [Ru(phen)₃]Cl₂ (**2**), [Ru(bpy)(phen)(bpg)]Cl₂ (**3**), and [Ru(dpq)₂(bxbg)]Cl₂ (**4**) where bpy is 2,2'-bipyridine, phen – 1,10-phenanthroline, bpg – bipyridine-glycoluril, dpq – dipyrido[3,2-*d*:2',3'-*f*]quinoxaline, and bxbg – bis(*o*-xylene)bipyridine-glycoluril are investigated. Rate constants have been measured by steady-state luminescence and phase-modulation fluorometry in aqueous solutions at different pH's. The rates for the oxidation of the phenols and phenolic aromatic amino acids spreads over a wide range from 4.2×10^9 to $6.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, depending on pH and the nature of solutes. At $\text{pH} > \text{pK}_a$ of the quenchers, the presence of reactive species (PhO^-) in the alkaline solutions is accounted for the rapid ET rates. In the pH range between 4 and 10 ($\text{pH} < \text{pK}_a$), the ETPT mechanism becomes dominant and the rate constants are relatively low. It reveals that the important parameters that influence the quenching reaction rates, others than the driving forces ΔG^0 are the steric and hydrophobic interactions arising from the structure of the compounds. This is clearly seen in the case of photoreaction between the Ru(phen)₃²⁺ complex and AcTyrOH. Phen ligands and acetyl group cause a steric effect, but strengthen the hydrophobic interactions and thus promote the quenching process. The pH-dependent equation of the observed rate constant for PhOH/AcTyrOH oxidation is expressed as a sum of rates for its protonated, neutral and deprotonated forms.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Oxidation of phenolic compounds partakes in many of the biologically important processes in nature. Oxidation of phenols in aqueous solution strongly depends on pH's because of their pH-dependence redox potentials [1]. Oxidation potential for phenol itself is reported as: $E_{\text{PhOH}^{\cdot+}/\text{PhOH}}^0 = 1.56 \text{ V vs. NHE}$ and for phenolate form is $E_{\text{PhO}^{\cdot-}/\text{PhO}^-}^0 = 0.85 \text{ V vs. NHE}$ [2]. To study the phenols oxidation reactions ruthenium polypyridyl complexes are usually used as favourable oxidants. Such excited state [Ru(bpy)₃]²⁺ ($E_{\text{Ru}^{2+}/\text{Ru}^{\cdot+}} = 0.84 \text{ V vs. NHE}$) or photogenerated [Ru(bpy)₃]³⁺ ($E_{\text{Ru}^{3+}/\text{Ru}^{2+}} = 1.26 \text{ V vs. NHE}$) [3] complexes with pH-independent reduction potentials are used for investigations of the phenols oxidation reactions in aqueous solutions. It is also reported that such phenol oxidations often involve a proton-coupled electron transfer (PCET) process as a function of pH. Hammarström et al. suggested an electron transfer – proton transfer (ETPT) at $\text{pH} \leq 4$

[2], concerted electron – proton transfer (CEP) between pH 4–10 and pure electron transfer (ET) at $\text{pH} > 10$ [4], as dominant reaction mechanisms between phenols derivatives and [Ru(bpy)₃]³⁺. Numerous experiments have been devoted to the phenols oxidation reaction by the [Ru(bpy)₃]²⁺ complex. However, most of the work focused on the reactions in strong basic solutions where the very reactive species (PhO^-) is present [5,6]. Oxidation of another type of the phenolic compounds, like tyrosine (TyrOH) amino acid also received scientist's great interest because of its function in Photosystem-II and as redox proteins. Hammarström's group focused on artificial photosynthesis and reported on a covalently linked [Ru(bpy)₃]²⁺-TyrOH system [7,8]. In such a system four mechanistic regions dominate over the wide pH-range including PTET at $\text{pH} < 5.5$, CEP between pH 5.5–8.5, PTET (proton transfer – electron transfer) between pH 8.5–10 and ET at $\text{pH} > 10$ [8]. Important effects/parameters that influence the phenols oxidation reaction rates are steric hindrance (distance), solvent (reorganization energy), coulombic charge, hydrogen bonding [4], hydrophobic interaction (π -stacking) and driving force (1).

As a contribution for an overview of the phenols oxidation reactions, the present work reports on the kinetics of the photoreaction between

* Corresponding authors.

E-mail addresses: truong.nguyenxuan@tugraz.at (T.X. Nguyen), grampp@tugraz.at (G. Grampp).

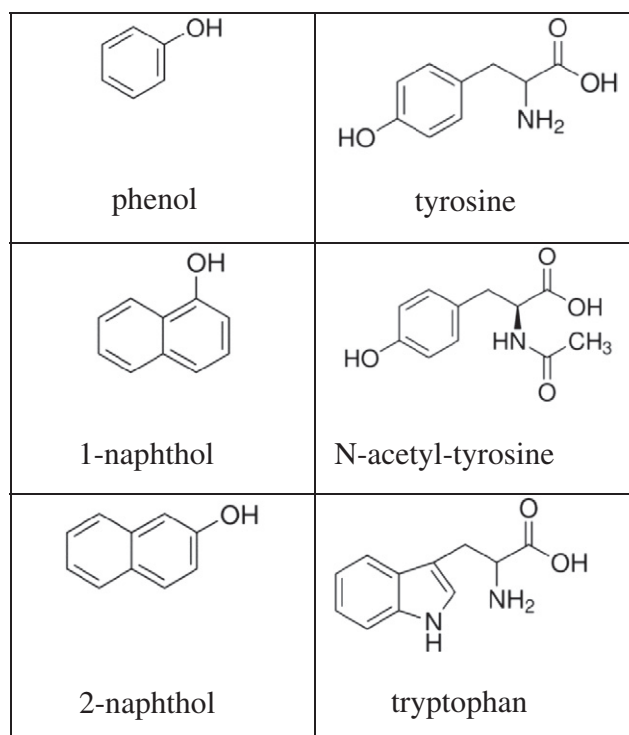
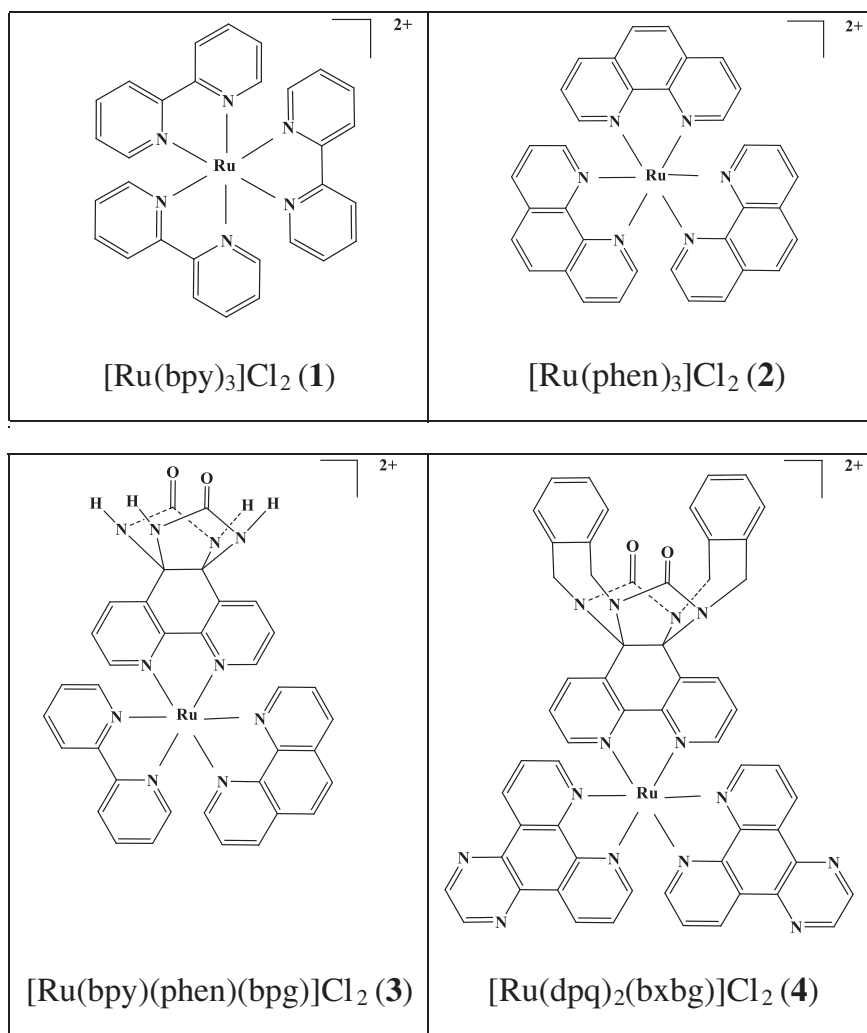


Chart 1. Molecular structures of compounds.

Download English Version:

<https://daneshyari.com/en/article/4754555>

Download Persian Version:

<https://daneshyari.com/article/4754555>

[Daneshyari.com](https://daneshyari.com)