Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Molecular Catalysis A: Chemical 251 (2006) 215–220
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Ru=O complexes as catalysts for oxidative transformations, including the oxidation of water to molecular dioxygen

Montserrat Rodríguez [a], Isabel Romero [a], Cristina Sens [a], Antoni Llobet [b,*]

[a] *Departament de Química, Universitat de Girona, Campus de Montilivi, E-17071 Girona, Spain*
[b] *Departament de Química, Universitat Autònoma de Barcelona, Bellaterra, E-08193 Barcelona, Spain*

Available online 20 March 2006

Abstract

This paper presents a short review related to the chemistry of the Ru=O group with data extracted from recent reports described in the literature by the authors of the present review and others. It was presented as an oral contribution to the 2005-Adhoc meeting held in Köln, Germany. The main thermodynamic characteristics of mononuclear complexes containing the Ru=O group are described and the effects produced by different type of electronic perturbations are analyzed through the ligands. Furthermore, an example of heterogenization of a Ru=O complex through a polypyrrol conductive polymer on a graphite electrode and its consequences are also described. Finally a description of complexes bearing two Ru=O groups is carried out with special attention to those complexes that in their higher oxidation states are capable of oxidizing water to molecular dioxygen.

Keywords: Ruthenium; Transition metal chemistry; Oxidation catalysis; Redox properties; High oxidation states; Polypyridylic ligands; Dinucleating ligands; Polynuclear complexes; Oxidation of water; Photosynthesis

1. Introduction

Ruthenium polypyridyl complexes have been extensively studied over the years because they enjoy a combination of unique chemical, electrochemical and photochemical properties [1] that has allowed to explore a wide variety of fields including photochemistry and photophysics [2], bioinorganics [3] and catalysis [4].

From a catalytic viewpoint Ru complexes have been shown to produce an extensive variety of transformations including: hydrogenation of double bonds, oxidation of organic substrates, isomerization reactions, nucleophilic addition to multiple bonds, carbon–carbon bond formation, CO_2 reduction, etc. [4a]. In the present paper we will describe the thermodynamic and reactivity properties of Ru complexes containing one and two Ru=O groups.

* Corresponding author.
E-mail addresses: montse.rodriguez@udg.es (M. Rodríguez), marisa.romero@udg.es (I. Romero), antoni.llobet@uab.es (A. Llobet).

1381-1169/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2006.02.008

2. Results and discussion

2.1. Complexes containing one Ru=O group

Over the last two decades a large body of ruthenium polypyridyl complexes containing the aqua ligand directly bonded to the metal has emerged [5]. The $[Ru(trpy)(bpy)(H_2O)]^{2+}$ (trpy = 2,2′:6′,2″-terpyridine and bpy = 2,2′-bipyridine) described by Meyer and co-workers [5a] constitutes a paradigm of this type of complexes both from a structural and a reactivity viewpoint (the structure of the ligands discussed in the present paper are presented in Chart 1). The higher oxidation states of this type of complexes are active catalysts for a variety of oxidative reactions such as the oxidation of alkenes to epoxides [6], sulfides to sulfoxides [7], phosphine to phosphine oxides [8], alchohols to aldehydes [9] and even saturated alkanes to alcohols [10]. Furthermore, from a bioinorganic perspective, they have also been shown to be able to selectively bind and cleave DNA molecules [11].

From a mechanistic perspective, it has been shown that the Ru=O group can oxidize substrates through a variety of reaction

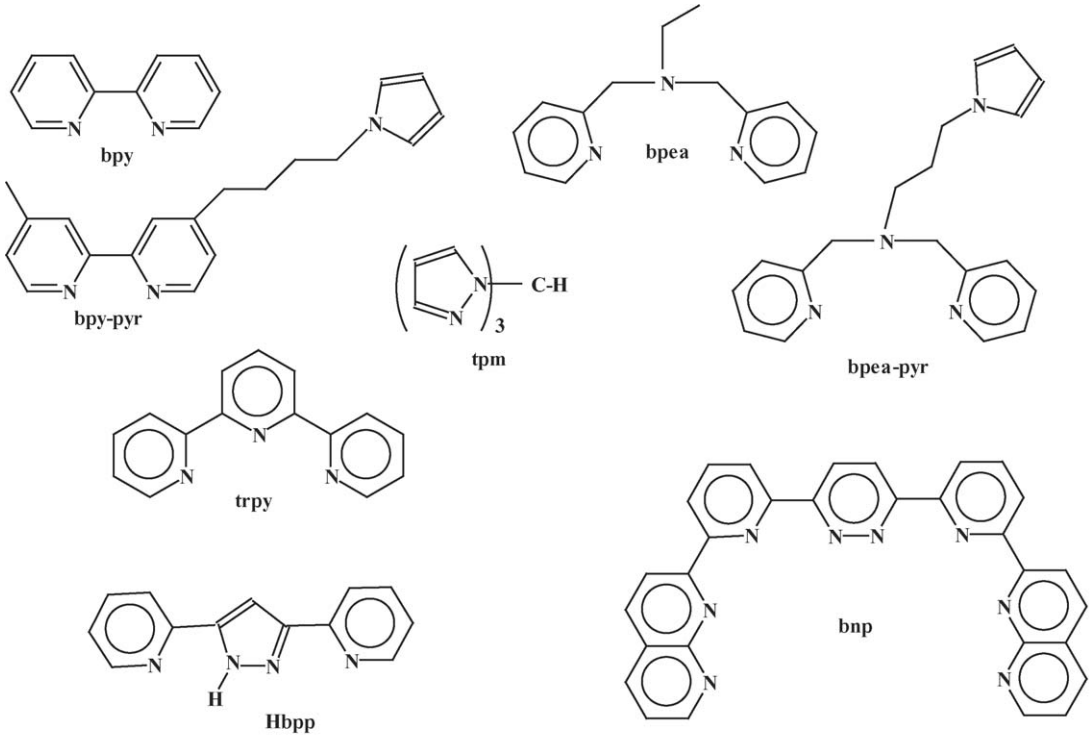

Chart 1. The ligands.

pathways. Those pathways depend on the oxidized substrate and include: outer sphere electron transfer, H-atom transfer, hydride transfer and oxygen atom transfer [1d].

2.1.1. Thermodynamic properties

The Ru(II)–H_2O complexes are of interest because their corresponding higher oxidation states can be reached within a relatively narrow potential range by sequential electron and proton loss, as shown in the Eqs. (1) and (2) for $[Ru^{II}(bpea)(bpy)(H_2O)]^{2+}$ (bpea is the tridentate ligand *N*,*N*-bis(2-pyridylmethyl)ethylamine) [4c]

$$[Ru^{II}(bpea)(bpy)(H_2O)]^{2+} \underset{+1H^+,+1e^-}{\overset{-1H^+,-1e^-}{\rightleftharpoons}} [Ru^{III}(bpea)(bpy)(OH)]^{2+} \quad (1)$$

$$E_{1/2}(Ru^{III/II}\text{at pH 7}) = 0.34\ \text{V versus SSCE}$$

$$[Ru^{III}(bpea)(bpy)(OH)]^{2+} \underset{+1H^+,+1e^-}{\overset{-1H^+,-1e^-}{\rightleftharpoons}} [Ru^{IV}(bpea)(bpy)(O)]^{2+} \quad (2)$$

$$E_{1/2}(Ru^{IV/III}\text{at pH 7}) = 0.46\ \text{V versus SSCE}$$

The Ru-OH_2 group is also of interest because of the oxidation state dependence of its acid–base properties as shown in Eqs. (3) and (4),

$$[Ru^{II}(bpea)(bpy)(H_2O)]^{2+} \underset{pK_{a,II}=11.1}{\rightleftharpoons} [Ru^{II}(bpea)(bpy)(OH)]^{+} + H^+ \quad (3)$$

$$[Ru^{III}(bpea)(bpy)(H_2O)]^{3+} \underset{pK_{a,III}=1.2}{\rightleftharpoons} [Ru^{III}(bpea)(bpy)(OH)]^{2+} + H^+ \quad (4)$$

All the thermodynamic properties are neatly represented in the corresponding Pourbaix diagram as shown in Fig. 1 for $[Ru^{II}(bpea)(bpy)(H_2O)]^{2+}$. Representative equations can be extracted from the diagram as shown in Fig. 2, for the same complex.

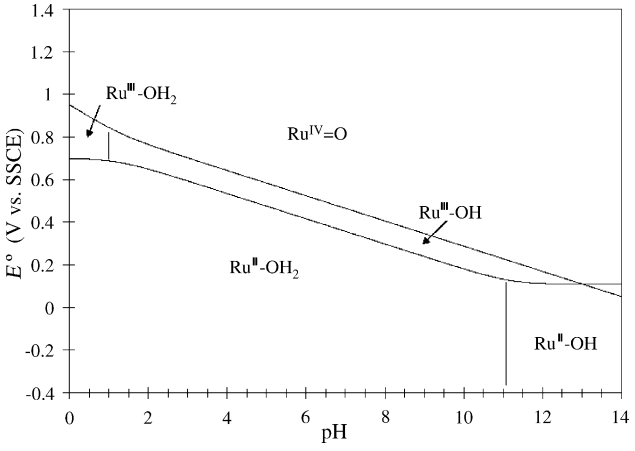

Fig. 1. $E_{1/2}$ vs. pH or Pourbaix diagram of $[Ru(bpea)(bpy)(H_2O)]^{2+}$. The pH-potential regions of stability for the various oxidation states and their dominant proton compositions are indicated by using abbreviations such as $Ru^{II}OH_2$, for example for $[Ru^{II}(bpea)(bpy)(H_2O)]^{2+}$. The p$K_a$ values are shown by the vertical solid lines in the various *E*–pH regions.