Inorganica Chimica Acta, 115 (1986) L33–L34

Acid-dependent Electrochemistry of Acetylacetonato-tetraammineruthenium

RAM SAHAI, ASHOK K. KABISATPATHY and JOHN D. PETERSEN*

Department of Chemistry, Clemson University, Clemson, S.C., 29634-1905, U.S.A.

(Received May 3, 1985; revised February 12, 1986)

There have been a variety of reports pertaining to pH dependent redox couples of ruthenium and osmium complexes [1, 2]. These systems are interesting because they not only allow pH control of redox reactions, but also can have implications ranging from controlled synthesis of polymetallic complexes as well as variability in potential for excited state electron-transfer processes [2].

Metal acetylacetonate complexes are components of active hydrogenation and hydrosilation Ziegler–Natta catalysts [3–5]**. Recently [6], it has been found that the reversibility of the reduction of a series of $M(acac)_n$ complexes is inversely proportional to the catalytic activity.

The following report describes the preparation of an acac complex of tetraammineruthenium, the absorption spectra of the various Ru(II) and Ru(III) species, and the pH dependent electrochemistry of the complexes.

Experimental

The synthesis of $[Ru(NH_3)_4(acac)](CF_3SO_3)_2$ required several intermediate preparations. The $[Ru(NH_3)_5Cl]Cl_2$ starting material was prepared as reported in the literature [7]. 1 g of $[Ru(NH_3)_5Cl]Cl_2$ was converted to the air stable $[Ru(NH_3)_5H_2O](TFMS)_3$ complex (HTFMS = trifluoromethanesulfonic acid) according to previous reports [8, 9].

Tetraammine(2,4-pentanedionato)ruthenium(III) trifluoromethanesulfonate was prepared by a modification of the preparation of tetraammine(2,2′-bipyrimidine)ruthenium(II) perchlorate [10]. A 195 mg sample of $[Ru(NH_3)_5H_2O](TFMS)_2$ was dissolved in 30 ml of 100% ethanol and was reduced with Zn(Hg) under argon. A 5–10 fold molar excess of acac in 10 ml of deoxygenated 100% ethanol was added and stirred for 3 h under argon. Within 30 min, the solution turned red and thereafter purple–red. The volume of the solvent was reduced to ~5 ml and excess of ether was added to precipitate the crude purple–red material. Following collection by filtration, the precipitate was recrystallized from acetone–CH_2Cl_2. The shiny purple crystalline material was filtered and dried under vacuum; yield 130 mg (76%). *Anal.* Calc. for $[Ru(NH_3)_4(acac)](CF_3SO_2)_2$: C, 14.8; H, 3.4; N, 9.9. Found: C, 14.3; H, 3.4; N, 10.1%. The infrared spectrum showed the characteristic acac peaks in the 1300–1500 cm^{-1} region. The Ru(II) derivatives were prepared *in situ* by adding Zn/Hg amalgam to a deoxygenated solution of the appropriate Ru(III) derivative. This absorption spectrum has been duplicated by electrolytic reduction of the Ru(III) species.

The electronic spectra for the various species reported here were recorded on a Bausch-Lomb Spectronic 2000 in water redistilled from alkaline permanganate in an all-glass apparatus. The cyclic and differential pulse voltammetric measurements were recorded on an IBM EC/225 Voltammetric Analyzer using IBM glassy carbon working, platinum auxiliary and saturated KCl/calomel electrodes. The buffers for the determination of the pH dependence of the redox potentials were prepared from 0.1 M solutions of H_3PO_4, KH_2PO_4, Na_2HPO_4, and Na_3PO_4. The pH values of the solutions were measured with an Orion F01A pH meter equipped with a Fisher combination glass/reference pH electrode.

Results and Discussion

The data from the electronic absorption spectra for the Ru(III) complex, $Ru(NH_3)_4(acac)^{2+}$ (**I**) and the two Ru(II) complexes, $Ru(NH_3)_4(Hacac)^{2+}$ (**II**) and $Ru(NH_3)_4(acac)^{+}$ (**III**) are listed in Table I. All three complexes display internal ligand bands in the ultraviolet region of the spectrum. In the visible region, the Ru(III) species (**I**) is dominated by a ligand-to-metal charge-transfer (LMCT) transition at 535 nm. The Ru(II) complexes (**II** and **III**) display metal-to-ligand charge-transfer (MLCT) bands at 533 and 452 nm, respectively.

The electrochemistry of the acac complexes shows a simple, reversible Ru(III)/Ru(II) couple over the pH range 2.6–14 with a $E_{1/2}$ value of −0.38 V *versus* SCE. Below pH 2.6, a proton-coupled redox process is observed between $Ru^{III}(NH_3)_4(acac)^{2+}$ and $Ru^{II}(NH_3)_4(Hacac)^{2+}$. Figure 1 illustrates this pH dependence which is Nerstian in behavior. Equations 1 and 2 describe the acid dependent electrochemistry observed for the system.

---

*Author to whom correspondence should be addressed.

**In this paper, acac refers to the monoanion of 2,4-pentanedione, $C_5H_7O_2^-$, while Hacac refers to the neutral molecule, $C_5H_8O_2$.

0020-1693/86/$3.50

© Elsevier Sequoia/Printed in Switzerland

TABLE I. Electronic Absorption Data for some Tetraammineruthenium(III) and -(II) Complexes of Acetylacetone[a]

Complex	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})	Assignment[b]
$Ru(NH_3)_4(acac)^{2+}$ (I)	737	291	LF
	537	1475	LMCT
	320	5129	IL
	281	9591	IL
$Ru(NH_3)_4(Hacac)^{2+}$ (II)	744	201	LF
	533	995	(MLCT?)
	480(sh)	812	–
	321	3948	IL
	281	6600	IL
$Ru(NH_3)_4(acac)^{+}$ (III)	452	3075	MLCT
	320(sh)	1330	IL
	275	8645	IL

[a] acac is the monoanion of 2,4-pentanedione; Hacac is the neutral molecule. [b] LF, ligand field (d–d); LMCT, ligand-to-metal charge transfer; MLCT, metal-to-ligand charge transfer; and IL, internal ligand (π–π^*).

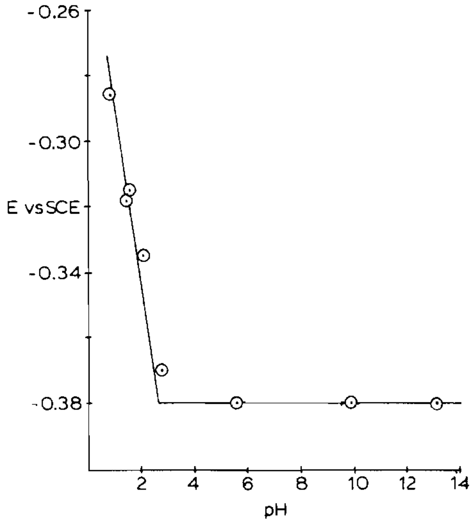

Fig. 1. Plot of the $E_{1/2}$ value for the Ru^{III}/Ru^{II} couple as a function of pH in 0.1 M buffered phosphate media.

$$Ru(NH_3)_4(acac)^{2+} + e^- \rightleftharpoons Ru(NH_3)_4(acac)^+ \quad (1)$$

$$2.6 \leqslant pH < 14$$
$$E_{1/2} = -0.38 \text{ } vs. \text{ SCE}$$

$$Ru(NH_3)_4(acac)^{2+} + e^- + H^+ \rightleftharpoons Ru(NH_3)_4(Hacac)^{2+} \quad (2)$$

$$E_{1/2} = -0.38 - \frac{RT}{nF} \text{ (pH = 2.6)}$$

The proton-coupled electron-transfer process is similar to that observed for $Co(acac)_3$ (pK_a 0.21–0.72 [10]). The pK_a of Hacac coordinated to $Ru(NH_3)_4{}^{3+}$ is ~2.6, which is far more acidic than the free ligand with a pK_a of 8.2 This is not surprising since the electron-withdrawing ability of $Ru(NH_3)_4{}^{3+}$ stabilizes the anion. In the pH range <2.6 the slope of the $E_{1/2}$ *versus* pH plot is 56 mv/pH units with a correlation coefficient of 0.98.

In the pH region of 2.6–14, the monoanionic form of acac is predominant for both Ru(II) and Ru(III). The electronic spectra is dominated by an LMCT band for the Ru(III) complex and an MLCT band for the Ru(II) complex . This type of excited state orientation presents interesting possibilities for a catalytic cycle in which photoreduction of the Ru(III) complex is coupled by photooxidation of the Ru(II) complex. Given the excited states associated with the metal complex oxidation states, the appropriate relay system could accomplish the above catalytic cycle.

Acknowledgement

The authors would like to acknowledge the Office of Basic Energy Research, Department of Energy for partial support of this research.

References

1 K. J. Takeuchi, M. S. Thompson, D. W. Pipes and T. J. Meyer, *Inorg. Chem.*, *23*, 1845 (1984) and refs. therein.
2 R. Sahai, W. R. Murphy, Jr. and J. D. Petersen, *Inorg. Chim. Acta*, in press.
3 B. R. James 'Homogeneous Hydrogenation', Wiley, New York, 1973.
4 M. F. Lappert, T. A. Nile and S. Takahashi, *J. Organomet. Chem.*, *72*, 425 (1974).
5 M. F. Sloan, A. S. Matlack and D. S. Breslow, *J. Am. Chem. Soc.*, *85*. 4014 (1963).
6 C. W. Anderson, K. R. Lung and T. A. Nile, *Inorg. Chim. Acta*, *85*, 33 (1984).
7 A. D. Allen, F. Bottomly, R. O. Harris, V. P. Reinsalu and C. V. Senoff, *J. Am. Chem. Soc.*, *89*, 5595 (1967).
8 D. M. Stanbury, O. Hass and H. Taube, *Inorg. Chem.*, *19*, 518 (1980).
9 S. E. Diamond and H. Taube, *J. Am. Chem. Soc.*, *97*, 5921 (1975).
10 R. R. Ruminski and J. D. Petersen, *Inorg. Chem.*, *21*, 3706 (1982).
11 N. A. Lewis and A. M. Roy, *Inorg. Chem.*, *23*, 3698 (1984).