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Ligand Effects on the Rate and Mechanism of Solvent Exchange at Rhodium(III) and Iridium(III)

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Abstract. The rate constants and activation parameters for solvent exchange for a series of Rh^{III} and Ir^{III} complexes of the form [M(H₂O)₆]³⁺ (M = Rh or Ir) and [Cp^{*}M(S)₃]²⁺ (M = Rh or Ir, and S = H₂O, MeCN, or Me₂SO) have been determined by NMR spectroscopy as a function of free-solvent concentration, temperature, and pressure, and the mechanisms for the respective exchange processes have been inferred.

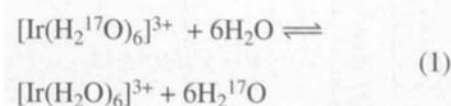
Introduction

Ever since the pioneering work of *Eigen* and *Wilkins* [1] which showed that, for aqueous solutions, the rates and activation parameters for ligand substitution were closely similar to those of solvent exchange, the study of the latter process has assumed fundamental importance. Accordingly, interest in the water exchange process has blossomed over the years resulting in one of the largest compilations of information about ligand substitution to date, and during this period, we have had the good fortune of being able to make significant contributions to this field of research [2]. The following report illustrates this fact by describing the results of several kinetic studies aimed at elucidating the factors which influence the water and/or solvent exchange processes at Rh^{III} and Ir^{III} metal centers.

Kinetics of H₂O Exchange for [M(H₂O)₆]³⁺ (M = Rh or Ir)

Amongst the earliest reported examples of solvent exchange kinetics was the work carried out by *Hunt* and *Taube* [3] on the hexaaquachromium(III) ion [Cr(H₂O)₆]³⁺. Their efforts established that this ion is capable of exchanging its bound

substitution. Thus, extreme temperatures were required to promote solvent exchange and this, in turn, lead to potential engineering or chemical problems (*i.e.*, [Ir(H₂O)₆]³⁺ was shown to be susceptible to oxidation and possibly oligomerization at high temperature) [5]. Using specifically designed high-temperature and high-pressure equipment, developed in-house, we were able to solve these problems, and in turn provide the first definitive quantitative study of the water exchange process on Ir^{III} [6]. Specifically, the exchange on [Ir(H₂O)₆]³⁺ (Eqn. 1) was followed by monitoring the



depletion of the hexaaqua ion and the enrichment of bulk water in ¹⁷O with time as a function of temperature and pressure; the resulting activation parameters are summarized in the *Table*. Notably, the rate constant obtained for water exchange on hexaaquairidium(III) ($1.1 \times 10^{-10} \text{ s}^{-1}$; residence time *ca.* 300 years) corresponds to the *slowest* water exchange at a homoleptic mononuclear metal center to date, and thus a further expansion of *Fig. 1*.

Furthermore, the kinetic values obtained for this exchange process are supportive of an associative interchange mechanism (I_a), as was also the case for the hexaaquarhodium analog.

H₂O with solvent, although the rate of this exchange was extremely slow. Subsequently, the hexaaqua ion of rhodium was shown to be even more inert, and kinetic parameters and solvent exchange mechanisms for both acidic Cr^{III} and Rh^{III} have now been proposed [4]. Interestingly, despite much effort, little is currently known about the kinetics of H₂O exchange for the third-row ion, namely the hexaaqua complex of Ir^{III}. This lack of kinetic information for [Ir(H₂O)₆]³⁺ was ascribed to its high degree of inertness toward ligand

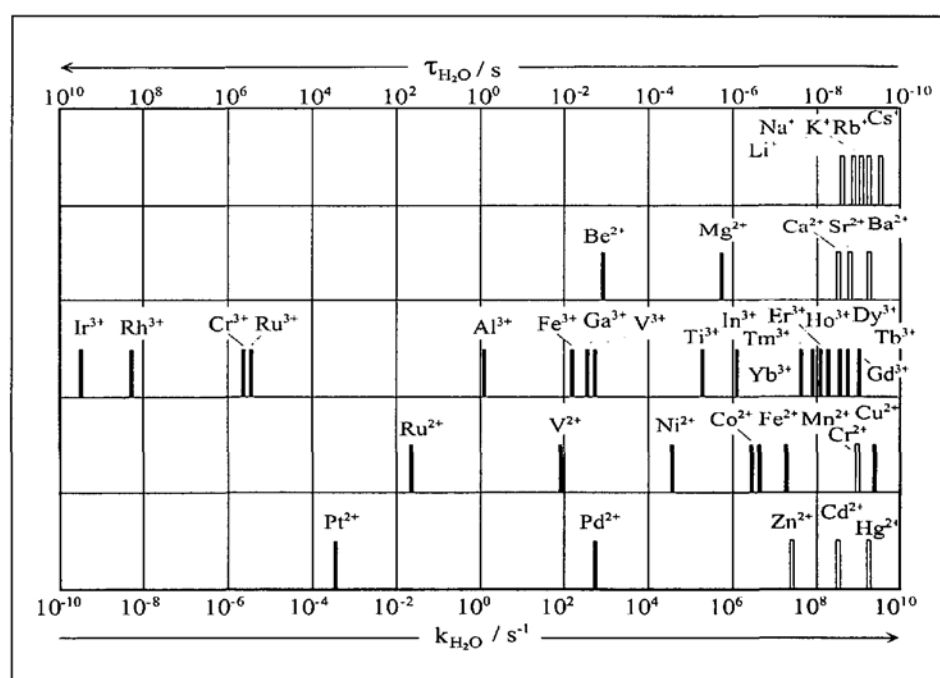


Fig. 1. Mean lifetimes of a particular H₂O molecule in the first coordination sphere of a given metal ion, $\tau_{\text{H}_2\text{O}}$, and the corresponding H₂O exchange rate constants, $k_{\text{H}_2\text{O}}$. The solid bars indicate directly determined values whereas the non-solid bars represent values deduced from complex-formation studies [6].

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Kinetics of H₂O Exchange for [Cp*M(H₂O)₃]²⁺ (M = Rh or Ir)

Interestingly, substitution of three ligated water molecules in the parent hexaqua complexes by a Cp*(η⁵-C₅Me₅) moiety (*i.e.*, [Cp*M(H₂O)₃]²⁺ where M = Rh or Ir) resulted in a dramatic 14-orders of magnitude increase in the respective H₂O exchange rate constants as measured by ¹⁷O-NMR by monitoring the relaxation rate (1/T₂^b) for the bound water signal as a function of temperature and pressure [7]; the activation values are presented in the Table. Of equal importance, the observed increase in the rate constants for the [M(H₂O)₆]³⁺/[Cp*M(H₂O)₃]²⁺ couples was also accompanied by an increase in dissociative character; the data being suggestive of a dissociative interchange mechanism (I_d) for both species (Fig. 2).

Kinetics of Non-aqueous Solvent Exchange for [Cp*Rh(S)₃]²⁺ (S = MeCN or Me₂SO)

Within the half-sandwich-geometrical framework, we have also successfully extended the kinetic studies to organic solvents. In particular, the solvent exchange on [Cp*Rh(S)₃]²⁺ (S = MeCN or Me₂SO) was investigated by ¹H-NMR line-broadening techniques as a function of free-solvent concentration, temperature, and pressure [8]; all activation values are found in the Table.

Following the solvent exchanges in the non-coordinating diluent CD₃NO₂ showed that the exchange rate constant was independent of the concentration of the free-solvent for both complexes, and thus inferred a rate law which was first order. Variable-temperature studies on [Cp*Rh(MeCN)₃]²⁺ and [Cp*Rh(Me₂SO)₃]²⁺ (Fig. 3) led to solvent exchange rate constants which are significantly slower than their aqua-ion analog (Table).

Furthermore, variable-pressure investigations on both these complexes provided small positive values for their respective volumes of activation which, like their aqua-ion partner, are consistent with a dissociative activation mode.

Conclusion

The rate constant obtained for the hexaqua complex of Ir^{III} corresponds to the slowest water exchange at a homoleptic mononuclear metal center to date. Substitution of three bound H₂O molecules in the parent hexaqua complexes (*i.e.*,

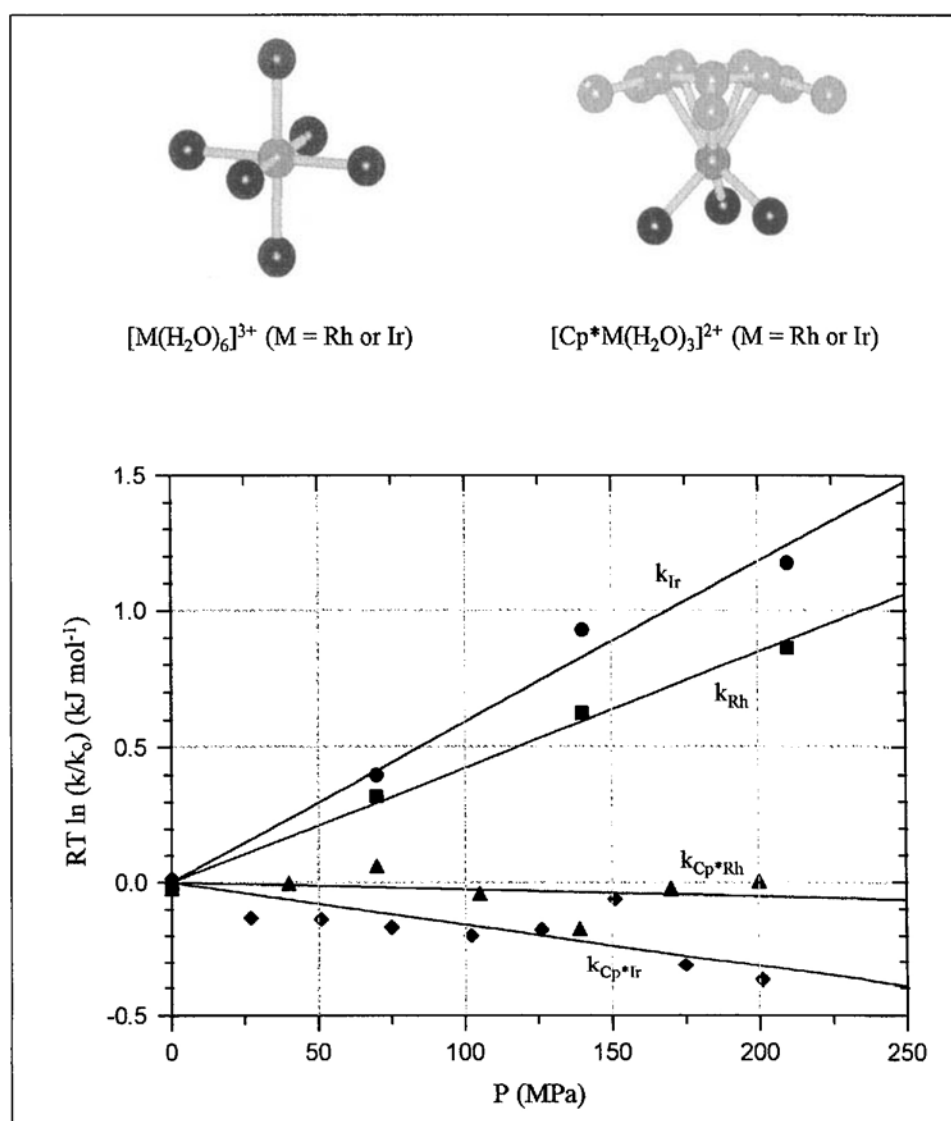


Fig. 2. Effect of pressure on the H₂O exchange rate constant for [M(H₂O)₆]³⁺ (M = Rh (at 323.2 K, ■) or Ir (at 358.2 K, ●)), and for [Cp*M(H₂O)₃]²⁺ (M = Rh (at 271.0 K, ▲) or Ir (at 281.0 K, ◆))

Table. Rate Constants and Activation Parameters for Solvent Exchange on Rh^{III} and Ir^{III} Solvates^{a)}

Solvate	k ²⁹⁸ [s ⁻¹]	ΔH [‡] [kJ mol ⁻¹]	ΔS [‡] [J mol ⁻¹ K ⁻¹]	ΔV [‡] [cm ³ mol ⁻¹]	Mech.
[Rh(H ₂ O) ₆] ^{3+ b)}	(2.2 ± 2.7) 10 ⁻⁹	131 ± 23	+29 ± 69	-4.2 ± 0.6	I _a
[Ir(H ₂ O) ₆] ^{3+ b)}	(1.1 ± 0.1) 10 ⁻¹⁰	130.5 ± 1	+2.1 ± 2	-5.7 ± 0.5	I _a
[Cp*Rh(H ₂ O) ₃] ^{2+ c)}	(1.6 ± 0.3) 10 ⁵	65.6 ± 7	+75 ± 24	+0.6 ± 0.6	I _d
[Cp*Ir(H ₂ O) ₃] ^{2+ c)}	(2.5 ± 0.1) 10 ⁴	54.9 ± 3	+24 ± 8	+2.4 ± 0.5	I _d
[Cp*Rh(MeCN) ₃] ²⁺	(3.8 ± 0.2) 10 ¹	75.4 ± 2	+38 ± 6	+0.8 ± 0.5	I _d , D
[Cp*Rh(Me ₂ SO) ₃] ^{2+ d)}	(3.6 ± 0.1) 10 ³	54.6 ± 0.3	+6.4 ± 1	+3.3 ± 0.1	I _d , D

^{a)} All values refer to the exchange of one particular solvent molecule. ^{b)} See [6]. ^{c)} See [7]. ^{d)} O-bonded exchange.

[Rh(H₂O)₆]³⁺ or [Ir(H₂O)₆]³⁺) by a Cp* moiety results in both a dramatic increase in the respective H₂O exchange rate constants and a change-over in mechanism of activation. The related organic solvates of Rh^{III} (*i.e.*, [Cp*Rh(MeCN)₃]²⁺ and

[Cp*Rh(Me₂SO)₃]²⁺) exhibit similar kinetic behavior to their aqua-ion analog, and in all three cases a dissociative mode of activation was inferred. However, within this half-sandwich framework, the rate of solvent exchange was found to decrease in the order H₂O > Me₂SO > MeCN.

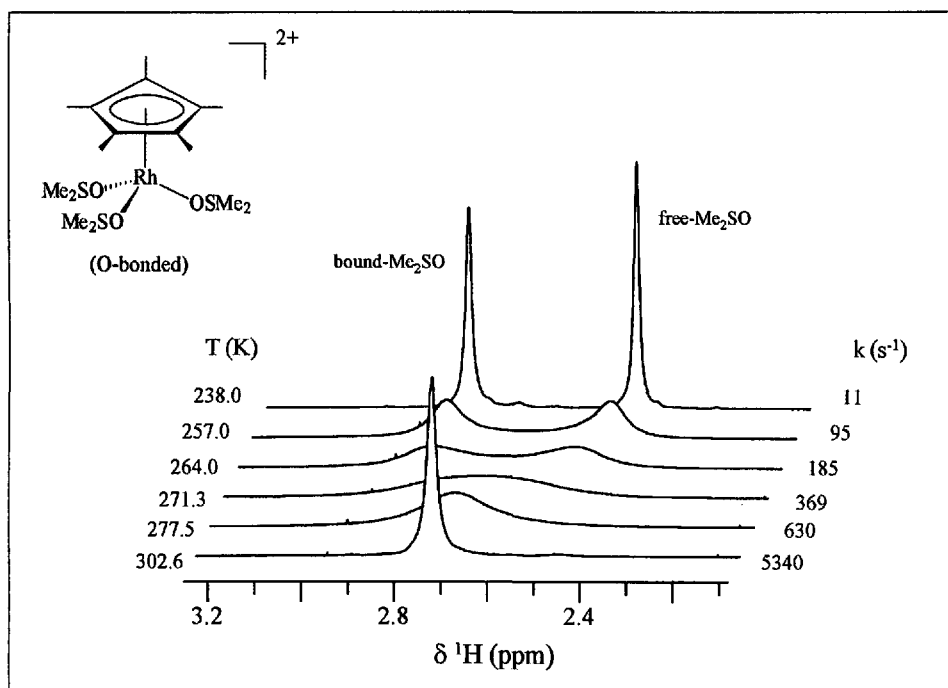


Fig. 3. Experimental $^1\text{H-NMR}$ (400 MHz) spectra of $[\text{Cp}^*\text{Rh}(\text{Me}_2\text{SO})_3](\text{PF}_6)_2$ (0.100 m) with free Me_2SO (0.304 m) in CD_3NO_2 at various temperatures

These results suggest that increasing the steric environment around the metal center promotes the dissociation process and thus leads to an increase in the rate of

solvent exchange whereas increasing the π -acceptor ability of the bound solvent ligand creates a stronger metal–ligand bond and thus decreases the exchange rate.

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Catalytic Opportunities in the Flavor and Fragrance Industry

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Abstract. Because catalytic processes produce in general less residues than conventional stoichiometric ones, they are advantageous for the environment. This short review will focus on new opportunities for catalysis in the field of terpene transformation, citral and ionones synthesis, and macrocyclic vs. aromatic musks.

Introduction

Like other chemical industries, the flavor and fragrance (F&F) industry [1][2] has taken up the challenge to reduce cost of waste treatment, thereby using processes more friendly for the environment. Thus, the substitution of conventional organic chemistry processes such as stoichiometric oxidation by permanganates and chromates, reduction by dissolving metals and metal hydrides, Wittig condensations (recycling of triphenylphosphine oxide),

Friedel-Crafts acylation, etc. by alternative cleaner, safer, and environmentally friendly alternative technologies are under continuously development. Most of the toxic metals such as chromium, lead, selenium, mercury, cadmium have been removed from industrial processes. The use of reagents such as acrolein, methyl vinyl ketone, phosgene, and dimethyl sulfate is severely limited because of transportation regulations, and/or have to be used at their production site. Chlorinated and aromatic solvents also have very re-

strictive uses. Perfume producers are also becoming more and more concerned with the biodegradability and innocuity of their products.

Catalysis is now seen as a substitute or a complement to conventional organic processes since it involves higher atom economy, and therefore generates much less waste, as has already been shown in the bulk chemical industry [3].

A further important feature of catalysis is enantioselectivity. Smell and taste involve chiral biological sensors that are sensitive to stereogenic centers in the molecules, and the organoleptic properties of two enantiomers often differ in intensity and quality [4]. For example, (+)-(*S*)-carvone (caraway-like) and (–)-(*R*)-carvone (spearmint-like) have different odors. Thus, enantioselective catalysis is the next frontier for the commercialization of chiral perfumes. This short review will deal with some recent applications of catalysis in the F&F industry, and focus on new opportunities in this area.

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