Kinetics of *cis*-[Ru(R-phen)(dcbH$_2$)(NCS)$_2$] formation: effect of the phenanthroline substituent on the rate of first intermediate formation

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Abstract

The [Ru(R-phen)(p-cymene)Cl] intermediate formation rate depends on the electron donating or withdrawing character of R.

Introduction

Ruthenium(II) *tris*-heteroleptic [Ru(L)(dcbH$_2$)(NCS)$_2$], L = polypyridyl ligand and dcbH$_2$ = 4,4'-dicarboxylic acid-2,2'-bipyridine have been employed as dye-sensitizers in DSSCs.[1,2] The synthesis of these compounds can be achieved by a one-pot procedure, starting from the precursor [Ru(p-cymene)Cl$_2$]$_2$ dimer and L in N,N-dimethylformamide (DMF), Figure 1.[3] In this work, the activation energies and formation rates of the [Ru(R-phen)(p-cymene)Cl] intermediate, phen = 1,10-phenanthroline and R = MeO, Me, Ph, H or Cl on its 4 and 7 positions, were evaluated in terms of the electron donating or withdrawing character of R.

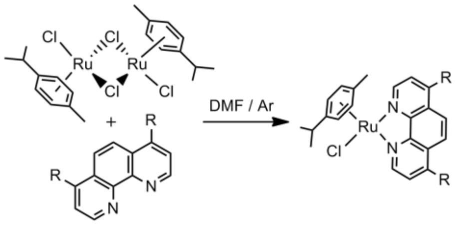

Figure 1. First step proposed for *cis*-[Ru(R-phen)(dcbH$_2$)(NCS)$_2$] formation.

Results and Discussion

Experiments were carried out in pseudo-first order in relation to [Ru(p-cymene)Cl$_2$]$_2$ and absorption changes were followed up to 20 min, from 15ºC to 30ºC. The observed rates (k_{obs}) determined for each experiment were plotted vs. [R-phen] to determine the second order rate constants (k_{so}), which was plotted vs. 1/T to result in the activation energies (E_a) The effect of the R groups was evaluated by plotting the E_a values vs. the Hammett constant (σ_p^+), Figure 2. Increase in E_a is observed as a function of σ_p^+. This trend can be correlated with a higher electron density on the nitrogen atoms of the ligand, which favors the coordination to the Ru(II) center. The k_{obs} vs. [R-phen] plots, Figure 3, demonstrate the rates dependence on the R substituent, which agree to an associative character mechanism.

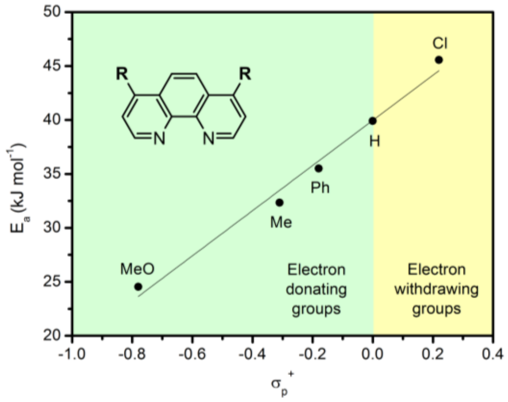

Figure 2. Activation energies of the intermediate [Ru(R-phen)(p-cymene)Cl] formation as a function of the σ_p^+ constant for the R substituent.

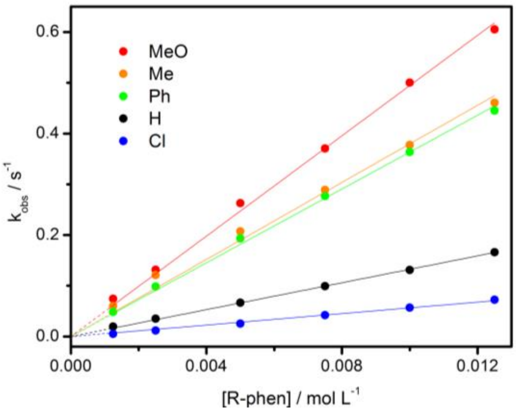

Figure 3. k_{obs} dependence on [R-phen]. T = 298 K.

Conclusions

The electron donating character of the substituent on the 4 and 7 positions of the 1,10-phenanthroline ring increases the basicity of the nitrogen atoms and consequently increases the reaction rates. The R-phen coordination is in accordance to an associative character mechanism.

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