

Activation parameters of $\text{cis-}[\text{Pt}(p\text{-FC}_6\text{H}_4)_2(\text{SMe}_2)_2]$

reaction with 1,10-Phenanthroline

Alireza Akbari* and Ali Samie

Department of Chemistry, Payame Noor University, 19395-4697 Tehran, Iran

E-mail: a_akbari@pnu.ac.ir

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Introduction

Ligand substitution reactions on monomeric square planar platinum (II) complexes have been extensively studied [1,2]. Some researchers have investigated and focused on the kinetics and mechanism of the interaction of platinum (II) complexes and bio-molecules with the aim of developing new family of metallo-pharmaceuticals [3,4]. Kinetics and mechanism of substitution and ring opening reaction of some platinum(II) complexes with *N*-heterocyclic bases have been studied by UV-Vis spectrophotometry [5].

Method & Results

Kinetics of the irreversible mentioned reaction was studied using UV-Vis spectrophotometry technique. The Eyring equation, and $K_{\text{obs}} = k_1 + k_2 [\text{Phen}]$, in which k_1 , k_2 and K_{obs} are the dissociative path, the associative and pseudo-first-order rate constants respectively, were used for calculations. The nonlinear curves of absorption against time of the reaction were analyzed with pseudo-first-order method and kinetic parameters, ΔH^\ddagger (K.J.mol⁻¹) and ΔS^\ddagger (J.mol⁻¹.K⁻¹), are estimated 28.677, 56.723 and -165.9, -72.2 in benzene and acetone respectively.

Conclusion

The extra stability of $\text{Cis-}[\text{Pt}(p\text{-FC}_6\text{H}_4)_2(1,10\text{-phenanthroline})]$ is related to chelate effect. The principal effect is the entropy, common in all chelate systems [6]. Considering that the platinum is an electron-rich metal and 1,10-phenanthroline has empty π^* orbital, yellow color in investigated solution could be due to the metal to ligand charge transfer (MLCT) [7]. The Pt-S is a soft-soft bond and on the other side, the Pt-C and Pt-N are soft-hard bonds. Consequently, according to the principle of symbiosis [8], the Pt-S is replaced by the Pt-N bond. Furthermore, *p*-FC₆H₄ is a π -acceptor and it can labialize the SMe₂ ligand. When such ligand forms strong π bond with Pt, the energy of the transition state is lower, and the activation energy is reduced [9]. As one can see, the parameters are almost the same and in fact, although we expected more dissociative path in benzene



(for substitution of bidentate ligand phenanthroline[10]), but a negative value of ΔS^\ddagger indicates that the associative path is current in benzene like acetone too.

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