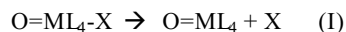


s9.m2.o5 **Reaction Pathways by Structure Correlation Methods: S_N1 Addition of Nucleophilic Ligands to Penta-coordinated V(IV) Oxo-Complexes.** V. Ferretti*, V. Bertolasi, P. Gilli, G. Gilli, *Dipartimento di Chimica and Centro di Strutturistica Diffraattometrica, Università di Ferrara, via L. Borsari 46, 44100 Ferrara (Italy); E-mail: frt@unife.it*

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Structure correlation methods applied to crystallographic database information may help understanding reaction pathways and properties that molecules display in any reaction environment of chemical relevance. The exact nature of the relationship between crystal structure correlations and chemical kinetics (or chemical equilibrium) is, however, a complex physico-chemical problem which has been seldom treated [1-3].

Most recently [4], the availability of experimental data on Re(V) and Tc(V) penta- and hexa-coordinated oxo-complexes (X-ray crystal structures, IR stretching frequencies, pK_a values of the ligand *trans* to M=O multiple bond, a few kinetic studies) has made possible to study the interdependence between thermodynamic stability (assessable from the pK_a values of the leaving ligand), structural properties and kinetic parameters for the dissociation reaction:



(M= Re, Tc; O=ML₄ = pentacoordinated oxo-complex; X= oxygenated leaving ligand).

Mathematical models of the reaction pathway have been proposed which, on the grounds of the Marcus rate-equilibrium theory [5], relate activation free energies, thermodynamic stabilities, and geometrical distances from the reaction transition state.

In the present communication we report on a similar study aimed at the mapping of the reaction pathway of the ligand dissociation (or association) reaction (I), in which O=ML₄ and O=ML₄-X are, respectively, V(IV) penta and hexa-coordinated oxo-complexes.

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