Notes

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 Diffrattometrica, Università di Ferrara, via L. Borsari 46, 44100 Ferrara (Italy); E-mail: frt@unife.it*
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Structure correlation methods applied to crys-tallographic database information may help under-standing reaction pathways and properties that molecules display in any reaction environment of chemical relevance. The exact nature of the relation-ship 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:

$$O{=}ML_4\text{-}X \rightarrow O{=}ML_4 + X \qquad (I)$$

(M= Re, Tc; $O{=}ML_4$ = 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 simi-lar study aimed at the mapping of the reaction pathway of the ligand dissociation (or association) reaction (I), in which $O{=}ML_4$ and $O{=}ML_4$-X are, respectively, V(*IV*) penta and hexa-coordinated oxo-complexes.

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