

THE NATURE OF THE Co-C BOND CLEAVAGE PROCESSES IN METHYLCOB(II)ALAMIN AND ADENOSYLCOB(III)ALAMIN

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In Memory of the Academician Constantin Turta

Abstract. Unfortunately, there are still significant disagreements between experimental and theoretical data of rate constants, energy barriers for Co-C bond cleavage process and coordination numbers of vitamin B₁₂ coenzyme species in spite of the remarkable efforts done by research community. Therefore, no grounded mechanisms for Co-C vitamin B₁₂ coenzyme bond breaking process and subsequent reactions have been found up to now. The influence of the mixing orbitals e.g. Pseudo-Jahn-Teller and similar effects on the reactions paths of bond-cleavage mechanisms of vitamin B₁₂ co-factors must be taken into account by utilizing multi-reference methods, in particular multi-configurational self-consistent field (MCSCF) method. Then, the change in total energy along the normal coordinate Q for the stretching mode including Co-C and Co-N bonds in vitamin B₁₂ cofactors is expected due to a “vibronic” coupling term, which couples an excited state and ground state by a second order derivative potential-energy operator. The strong state mixing effect is expected to lead to low energy barriers and to Co-C and Co-N axial bond cleavage events in agreement with experimental data. Afterward, the updated mechanisms of vitamin B₁₂ bio-processes can be determined.

Keywords: vitamin B₁₂, mechanism, bio-catalysis, Pseudo-Jahn-Teller effect, DFT, MCSCF.

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