

## WHAT DETERMINES THE NATURE OF HYDROGEN ATOMS ON M<sup>o</sup> SURFACES?

### M<sup>o</sup>-NANOPARTICLES CATALYZE THE REDUCTIVE DE-HALOGENATION OF HALO-ORGANIC COMPOUNDS BY BH<sub>4</sub><sup>-</sup> IN AQUEOUS MEDIA.

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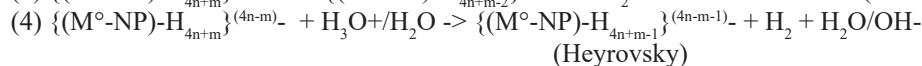
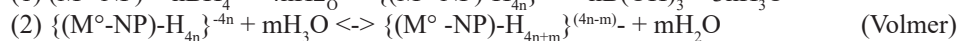
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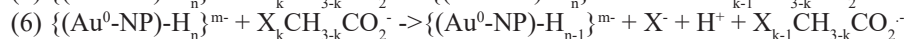
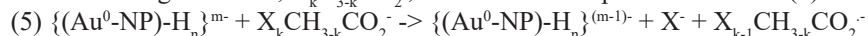
The mechanisms of formation of M<sup>o</sup>-NPs (nano-particles) via the reduction of M<sub>aq</sub><sup>nt</sup> by weak reducing agents is considerably more complex than usually considered.

M<sup>o</sup>-NPs catalyze the reaction of BH<sub>4</sub><sup>-</sup> with water to form hydrogen:



Isotopic labeling experiments point out that the mechanism of the process observed depends on [BH<sub>4</sub><sup>-</sup>]: The higher the concentration the relative contribution of the Heyrovsky mechanism increases and that of the Tafel decreases. Surprisingly the rate constant  $k_2$  is slow. The relative contributions of the two mechanisms differ considerably for M<sup>o</sup> = Au<sup>o</sup> and Ag<sup>o</sup>.

When halo-organic acids, X<sub>k</sub>H<sub>3-k</sub>CO<sub>2</sub><sup>-</sup>, X = Cl or Br are present reactions (5) and/or (6) compete with reactions (2) - (4).



These reactions are followed by reaction (7):



The mechanisms of decomposition of the transients  $\{(Au^0-NP)-H_n\}-CX_{k-1}H_{3-k}CO_2^{m-}$  thus formed depends on [BH<sub>4</sub><sup>-</sup>] in an analogous way to that reported above. It depends also on the nature of M<sup>o</sup> and X.