ON THE MECHANISM OF ETHYLENE AND PROPYLENE INSERTION INTO METAL-HYDROXO BONDS

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The process of olefin insertion is suggested to be accompanied by $M-\text{IC}$ bond dissociation (rate-determining step) with further formation of a bond with the fifth ligand $L$ and the transfer of a hydride ion from one carbon atom to the other.

Ethylene insertion into the metal-hydroxo bond is known to be one of the steps in ethylene oxidation by acidocomplexes of Pd(II) in aqueous media. There are conflicting views on the occurrence of this reaction via trans or cis ethylene and hydroxo ligands and on the composition and structure of the intermediate and the transition state /1-14/.

The aim of the present study was to construct a model for the cis- or trans-addition of ethylene and propylene to the metal-hydroxy bond:

$$[\text{MX}_2(\text{C}_n\text{H}_{2n})\text{OH}]^- \rightarrow [\text{MX}_2L(\text{C}_n\text{H}_{2n}\text{OH})]^{2-}$$

($M = \text{Pd, Pt}$) in terms of the interacting bonds method (IBM) /15/.

*Description of the model.* In terms of the IBM the atomization energy of the multiatomic system is described as:

$$H_{at} = \sum_i \nu_i (2 - \nu_i) E_i - \sum_{i > k} \nu_i \nu_k \Delta_{ik}$$

Here $E_i$ and $\Delta_{ik}$ are semiempirical parameters for the strength of the $i$-th bond and the interaction between the $i$-th and $k$-th bonds meeting on one atom, respectively. Bond coefficients $\nu_i$ are determined from the condition of the maximum $H_{at}$. The dependence of $\Delta_{ik}$ on the angle between the bonds was taking
into consideration as

$$\Delta_{ik} = \Delta_0 / [\sin(\theta_{ik}/2)]$$

where $\theta_{ik}$ is the angle between the i-th and the k-th bonds, $\Delta_0^{\text{trans}} = \sqrt{2} \Delta_0^{\text{cis}} = 77.7$ and $51.4$ kJ/mol for Pd and Pt, respectively. The latter values were obtained from the heats of metal atomization /16/, taking into account the relationships $E_{M-M} = 4.3 \Delta_M /17/$. Values of the parameters applied for the calculations:

- $E_{C-C} = 607.8$, $\Delta_C = 141.3$, $E_{Pd-C} = 429.7$, $E_{O-H} = 585.2$, $E_{Pt-C} = 449.4$, $E_{Pt-O} = 393.3$, $E_{Pd-O} = 349.4$, $\Delta_0 = 313.5$, $E_{C-O} = 518.3$, $E_{Pt-Cl} = 376.2$, $E_{Pt-Br} = 329.0$, $E_{Pt-J} = 272.1$, $E_{Pd-Cl} = 334.4$, $E_{Pd-Br} = 289.7$, $E_{Pd-J} = 236.2$

were determined from the formation heats of the compounds containing a given bond (hereinafter all values are given in kJ/mol).

In the initial state of cis (1) and trans (2) addition, the plane of H$_2$C-M-CH$_2$ is positioned normal to that of the complex:

The angle $\theta$ for ethylene estimated in terms of geometry /18/ equals $37.2^\circ$; for propylene it is assumed to be the same.

It is suggested that in the transition state of addition, the M ion is five-coordinate and its coordination sphere is of a trigonal bipyramidal structure with angles of $120^\circ$ between the bonds in the equatorial plane. It is also suggested that during the formation of the five-coordinate state, the parameters $\Delta_0$ do not change. Hence, the interactions in the equatorial plane and also between the axial ligands are characterized by the value of $\Delta_0^{\text{trans}}$, whereas those between the equatorial and axial ligands are determined by the $\Delta_0^{\text{cis}}$ parameter.

**Method for estimating the activation energy of addition.** If the activation consists in the dissociation of some bond, the problem reduces to the calculation of the difference in the energies of the initial (involving a given bond) and the final (with a dissociated bond) states. However, if the activation involves both dissociation and formation of new bonds, a concept of the „valence-restrained” atom where all dis-