CALORIMETRIC STUDY OF THE OXOTRANSFER PROCESS INVOLVING TRIPHENYLPHOSPHINE AND A MOLYBDENUM-CONTAINING ANALOGUE OF THE ENZYME ACTIVE SITE

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The key process that forms the basis of molybdenum enzymes' operation is oxotransfer, i.e. the transfer of an oxygen atom between the enzyme's active site and the substrate. Molybdenum complexes with dithiolene ligands are commonly used as convenient models of the active site in molybdenum-containing enzymes. Research on these model active sites typically aims to obtain kinetic and electrochemical characteristics of the system. Nevertheless, thermodynamic data are essential for identifying the driving force behind the oxotransfer process [1].

In this study, the molybdenum complex with maleonitriledithiolate ligand (mnt^{2-}) of the composition $(Bu_4N)_2[MoO_2(mnt)_2]$ was used as a model of the enzyme active center, and triphenylphosphine PPh_3 was used as the substrate. The calorimetric study was performed using Calvet-type microcalorimeter (KYV) [2] to obtain data on the change in enthalpy during the dissolution processes of the solid sample $(Bu_4N)_2[MoO_2(mnt)_2]$ (a) in pure acetonitrile and (b) in acetonitrile containing a portion of PPh_3. Subsequently, the total changes in enthalpy upon interaction of the components in the liquid phase were calculated.

By varying the ratio of the complex to the substrate, the values of the total thermal effects during the oxotransfer process in this system were obtained. The increase in the phosphine quantity in the system leads to a significant increase in total the thermal effect. These data indicate a catalytic character of the process, which correlates with the nature of the synthetic model.

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2. Golubev B.A., Kondratev Yu.V., and Sheitelman B.I. (1985) USSR Inventor's Certificate no. 1283553.

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