

Photophysics and photochemistry of haloid Pt(IV) complexes

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The photochemistry of Pt(IV) complexes has attracted attention for more than half a century. The haloid Pt(IV) complexes display high photochemical activity^[1-17] which can find an application in different technologies. The photochemistry of Pt(IV) complexes is of special interest due to the possibility of effective and fast photosynthesis of new Pt(II) complexes for the searches of anticancer platinum compounds.^[5-8] Due to these reasons, the determination of fast primary processes in photochemistry of these complexes is of considerable interest. Our studies by laser flash photolysis and cw methods^[1-4] have shown that there operate several mechanisms in photochemistry of PtCl₆²⁻ and PtBr₆²⁻ complexes. In the report it will be shown that in organic solvents the main mechanism of photochemical reactions for PtCl₆²⁻ complex is the electron transfer from RH molecules with the formation of such primary particles as the PtCl₆³⁻...R• radical complexes.

The formation of intermediate Pt(III) complexes allows to introduce the desirable organic or bioorganic ligands into labile coordination sphere of Pt(III) ion and to obtain new Pt(II) complexes.^[5-8] It will be presented the nature and reactions of intermediates in photochemistry of Pt(IV) complexes in solutions at room temperatures and in frozen matrices. The detection of the optical and ESR spectra during the photolysis of PtCl₆²⁻ and PtBr₆²⁻ complexes in the frozen methanol matrix made it possible to measure the relative yields of the intermediate radical species. The results obtained show that the final products (PtCl₄²⁻ and PtBr₄²⁻ complexes) is formed by two electron transfer from the solvent molecules even in a low temperature matrix. The transfer of the first electron is photoinitiated, and the second electron is transferred under dark conditions.^[2, 9]

It will be shown that in aqueous solutions the excitation of complexes often leads to the appearance of water molecule in coordination sphere.^[10, 12, 13] The UV photolysis of PtCl₆²⁻ in aqueous solutions leads to its photoaquation with a quantum yield of 0.19. Laser flash photolysis experiments (308 nm) provided evidence of the formation of Pt(III) intermediates and Cl₂^{•-} radical anions. The Pt(III) complexes formed as a result of an intrasphere electron transfer from Cl⁻ ligands to the excited Pt(IV) ion. However, the main (~90%) photolysis channel was not accompanied by the transfer of Cl atoms to the solvent bulk. The photoaquation of PtCl₆²⁻ results from the back electron transfer in the secondary geminate pair, [PtCl₅(H₂O)]²⁻ - atom •Cl.

In addition we will show the ultrafast photophysical processes for these complexes lie in the femto and picosecond time intervals.^[11, 15] Ultrafast pump-probe spectroscopy (420 nm) was applied to study the photoaquation of PtBr₆²⁻ complex. The excitation to d-d excited ¹T_{1g} state was followed by the formation of an intermediate absorption decaying with characteristic times of 370 fs, 2.2 and 15.2 ps. Two shorter times were attributed to the formation of the lower excited state (³T_{1g}) and its vibrational cooling accompanied by solvent relaxation. The longest time was interpreted as ³T_{1g} transition to the hot ground state (¹A_{1g}) and the dissociation product (PtBr₅(H₂O)⁻ complex). The key fast reaction for PtCl₆²⁻ complex is the

inner-sphere electron transfer, which results in an Adamson radical pair that lives for several picoseconds, and the subsequent photoaquation in aqueous solutions and photoreduction in alcohols. The chlorine atom formed as the primary product escapes the solvent cage in aqueous solutions or oxidizes a solvent alcohol molecule via secondary electron transfer, producing secondary intermediates that react on the microsecond time scale.

Thus, the report will present the results of studies of photophysical and photochemical processes for PtCl_6^{2-} and PtBr_6^{2-} complexes in a time scale from hundreds of femtoseconds to milliseconds and in a temperature range from a solution at RT to frozen at 77 K matrices.

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