

Photochemistry of hexachloroosmate complex in aqueous and ethanolic solutions

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Studies on the photochemistry of noble metal complexes are needed to understand the processes occurring in photocatalysis and photodynamic therapy of malignant tumors. Electronic configuration of osmium atom ensures the existence of conditions in the oxidation states of +8 to -2, provides a rich photochemistry of its compounds. However, information on the photochemistry even the simplest complex OsCl_6^{2-} [1, 2] is obviously incomplete.

We have studied the photochemistry OsCl_6^{2-} complex in aqueous and ethanolic solutions. We used the methods of stationary photolysis, nanosecond laser flash photolysis and ultrafast kinetic spectroscopy (temporal resolution of 100 fs, excitation in the region of 400 nm).

OsCl_6^{2-} photolysis in water and ethanol solution is a multi-step. The first step is photosolvation forming $\text{OsCl}_5(\text{H}_2\text{O})^-$ (or $\text{OsCl}_5(\text{C}_2\text{H}_5\text{OH})^-$). Prolonged irradiation of aqueous solutions leads to further photoaquation. In alcohols occur parallel processes - photosolvation and photoreduction.

It was found that photosolvation process is fully completed within 100 ps. Registered key intermediate having an intense absorption in the region 450-650 nm (see Figure 1). As a result of quantum chemical calculations intermediate was interpreted as lower electronically excited (triplet) state of the original complex or five-coordinate complex of Os(IV) - $^3\text{OsCl}_5^-$. The observed processes are interpreted as the transition of the excited Franck-Condon state to the key intermediate (characteristic time of 300 - 400 fs), the vibrational relaxation (2.5 - 3 ps) and the transition to the ground state and the reaction product (30-40 ps).

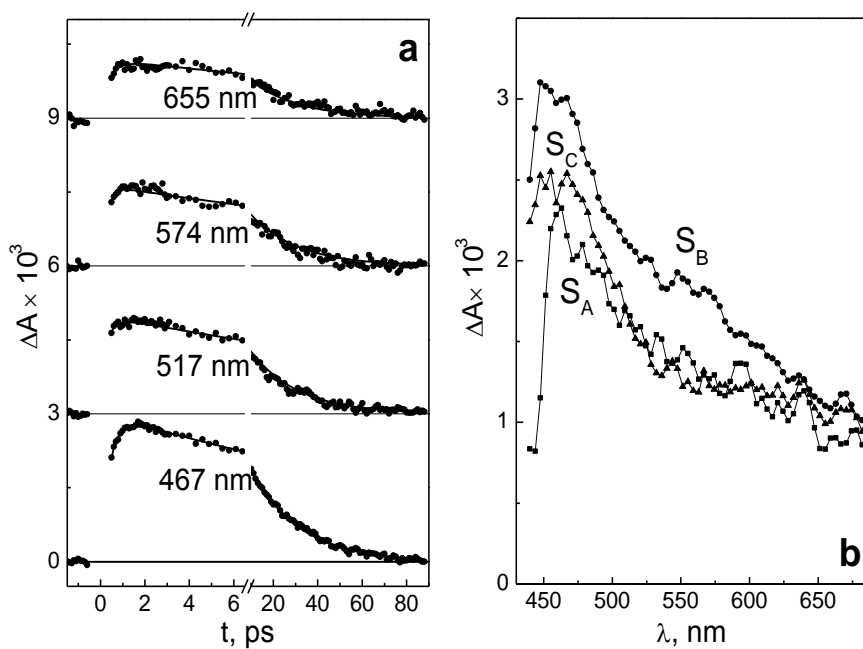


Figure 1. The results of ultrafast kinetic spectroscopy (**a** - kinetic curves and fitting, **b** – SADS corresponding to model $\text{OsCl}_6^{2-} \xrightarrow{h\nu} \text{A} \rightarrow \text{B} \rightarrow \text{C} \rightarrow (\text{OsCl}_6^{2-} + \text{products})$)

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References:

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