

Fast Photophysics Processes and Transient Species in Photochemistry of Ni(S₂P(i-Bu)₂)₂ Complex in CCl₄

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Femtosecond spectroscopy and nanosecond laser flash photolysis were used to study the photophysical and photochemical transformations of bis-diisobutyl-dithiophosphinate Ni(II) complex (Ni(S₂P(i-Bu)₂)₂) in CCl₄ solutions [1]. The radiation of second harmonic (405 nm) of Ti:Sapphire laser transfers Ni(dtpi)₂ complex to excited CTLM state. Its decay in CCl₄ is described by two exponents with times 0.58 and 2.0 ps. The first process involves the fast transitions from CTLM state to lower-lying (*d, d*)^{*} state and then to "hot" ground state. The second time corresponds to the vibrational cooling of this "hot" ground state.

The study of photochemistry was performed with laser flash photolysis at 308 nm. In this case an electron transfer from the excited Ni(dtpi)₂ complex to a solvent molecule leads to the appearance of primary intermediate, the [ClNi(dtpi)(^{*}dtpi)] complex, in which a ^{*}dtpi radical is coordinated with a nickel ion via one sulfur atom. In fast reaction with Ni(dtpi)₂, this complex forms a long-lived dimer ClNi(dtpi)(^{*}dtpi)[Ni(dtpi)₂] (Fig. 1). This intermediate for a few hundred microseconds decays in the reaction of recombination with the formation of (dtpi)₂ disulphide and ClNi(dtpi) complex. The quantum chemical calculations allowed to determine the geometry of the intermediate complexes arising in the photochemistry of Ni(S₂P(i-Bu)₂)₂ complex.

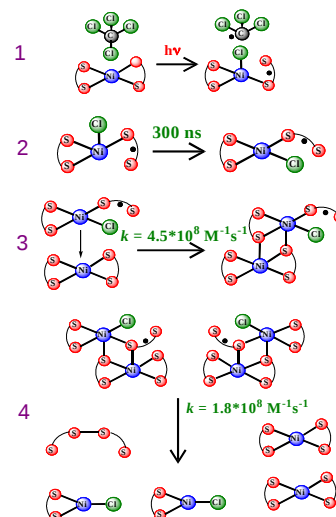


Fig. 1. Scheme of photochemical transformation of Ni(S₂P(i-Bu)₂)₂ complex in CCl₄.

- (1) Excitation of Ni(S₂P(i-Bu)₂)₂ complex and electron transfer to CCl₄ molecule;
- (2) Change of geometry of Cl_{ax}Ni^{II}(dtpi)(^{*}dtpi) complex to Cl_{eq}Ni^{II}(dtpi)(^{*}dtpi) state;
- (3) Reaction of Cl_{eq}Ni^{II}(dtpi)(^{*}dtpi) and initial Ni(S₂P(i-Bu)₂)₂ complex resulting in ClNi^{II}(dtpi)(dtpi^{*}) [Ni^{II}(dtpi)₂] dimer formation;
- (4) Final reaction of two ClNi^{II}(dtpi)(^{*}dtpi)[Ni^{II}(dtpi)₂] dimers resulting in the formation of final products.

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[1] A.I. Solovyev, A.V. Mikheyliis, V.F. Plyusnin, A.A. Shubin, V.P. Grivin, S.V. Larionov, N.V. Tkachenko, H. Lemmetyinen, *J. Photochem. Photobiol. A: Chem.*, **2019**, *381*, p. 111857.