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Preparation of Platinum(II) Cyclooctadiene Complexes by Photoirradiation

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Abstract—Preparation of platinum cyclooctadiene complexes under photoirradiation was studied, and the reaction mechanism was suggested.

It was shown previously [1, 2] that heating of platinum(II) disulfoxide complexes in a solution containing excess cycloocta-1,5-diene (COD) results in the formation of dichloro(cycloocta-1,5-diene)platinum(II), $[Pt(COD)Cl_2]$, in a high yield. This complex was formed most readily when starting from (–)-*cis*-$[Pt(Me\text{-}p\text{-}TolSO)_2Cl_2]$ (Me-*p*-TolSO is methyl *p*-tolyl sulfoxide). The chirality of the complex allowed the reaction progress to be monitored by optical rotation, as the rotation of the reaction mixture changed sing owing to consumption of the (–)-complex and formation of the (+)-ligand [2].

$$(-)\text{-}cis\text{-}[Pt(Me\text{-}p\text{-}TolSO)_2Cl_2] + COD$$
$$\rightleftarrows [Pt(COD)Cl_2] + 2(+)\text{-}Me\text{-}p\text{-}TolSO.$$

On the other hand, the photoirradiation of sulfoxide-containing platinum(II) complexes of a *cis* structure causes their isomerization into a photochemically inactive *trans* form [3, 4], which proceeds through elimination of the free sulfoxide [4]. This fact allowed us to expect the positive effect of photoirradiation on the replacement of sulfoxide by COD.

We found that the irradiation of a mixture of (–)-$[Pt(Me\text{-}p\text{-}TolSO)_2Cl_2]$ isomers (the complex exists in solution as an equilibrium mixture of 14.4% *trans* and 85.6% *cis* forms [5]) in methylene dichloride in the presence of a tenfold molar excess of COD accelerates the variation of the observed rotation angle of the reaction mixture (Fig. 1, curve *1*). The rate of variation of the rotation angle upon irradiation through quartz is ~14 times higher than without it (40 min after the start of the reaction, 25°C). This results from the replacement of the sulfoxide by cyclooctadiene (Fig. 1, curve *2*) and from the concurrent *cis–trans* photoisomerization of the complex (Fig. 1, curve *3*). As the irradiation is stopped, the reverse *trans–cis* isomerization starts, until an equilibrium mixture of the isomers is formed (Fig. 1, curve *3*). The replacement rate after preirradiation is 1.5 times higher (after 120 min) than without irradiation (Fig. 1, curves *2* and *4*), but much lower than during the photoactivation.

Thus, the rate of the formation of the cycloalkene complex is higher under irradiation than during the subsequent keeping of the reaction mixture in the dark. This is due to the fact that, under the conditions of

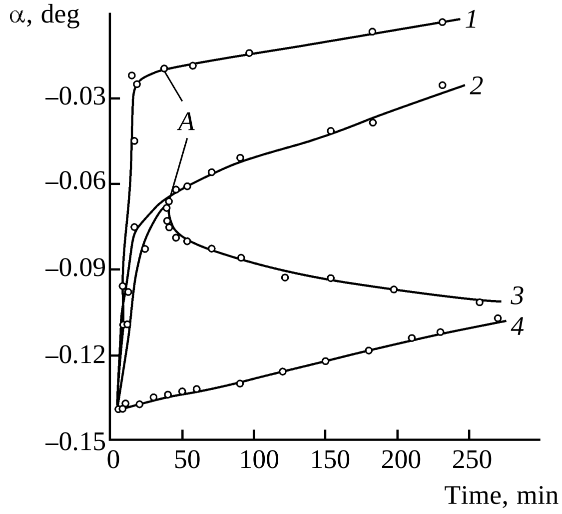

Fig. 1. Variation with time of the observed rotation angle (α) of the reaction mixture (25°C, c_c 1.8×10^{-3} M): (*1*) reaction of (–)-*cis*-$[Pt(Me\text{-}p\text{-}TolSO)_2Cl_2]$ with COD (molar ratio of reactants 1 : 10, irradiation for 41 min, quartz); (*2*) calculated curve for the reaction of (–)-*cis*-$[Pt(Me\text{-}p\text{-}TolSO)_2Cl_2]$ with COD, corrected for isomerization (the result of subtracting curve *3* from curve *1*; (*3*) irradiation of (–)-*cis*-$[Pt(Me\text{-}p\text{-}TolSO)_2Cl_2]$ in the absence of COD (irradiation for 41 min, quartz); (*4*) reaction of (–)-*cis*-$[Pt(Me\text{-}p\text{-}TolSO)_2Cl_2]$ with COD (molar ratio of reactants 1 : 10, without irradiation). (*A*) Instant of switching off the irradiation.

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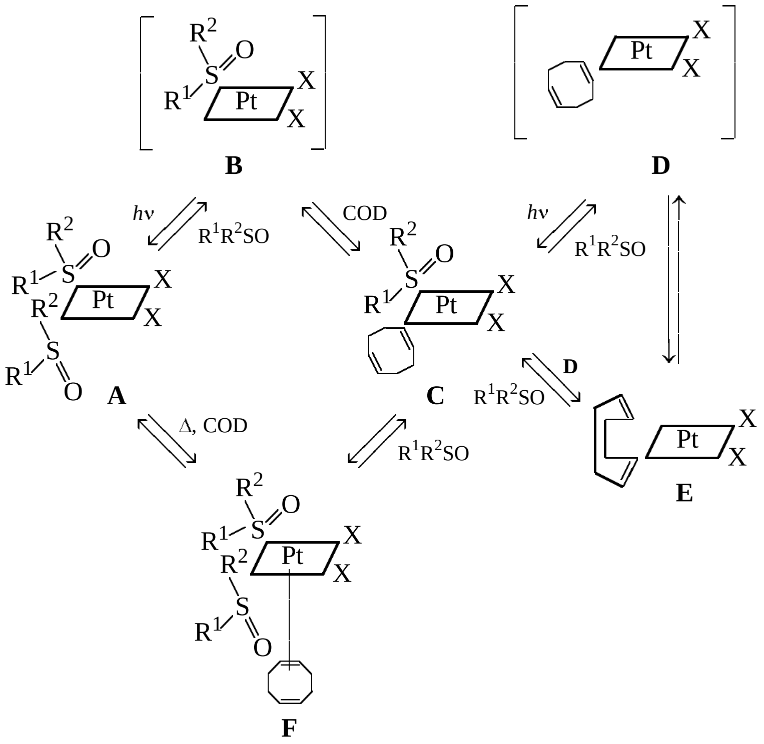
photolysis, sulfoxide is replaced by COD by another mechanism than in the thermal reaction.

The photolysis of the disulfoxide complex **A** results in the dissociation of the Pt–S bond with the formation of the free sulfoxide and a coordination-unsaturated platinum intermediate, which, in turn, instantaneously reacts with COD to give complex **B**. We failed to detect an intermediate of such a structure by ^{1}H NMR spectroscopy [2]; however, Sanger [6] reported on the formation of a rhodium complex containing η^2-cyclooctadiene.



The resulting complex **C** eliminates the second sulfoxide molecule under the action of the next light quantum, yielding coordination-unsaturated short-lived complex **D** which is immediately stabilized by an intramolecular conversion to give reaction product **E**.

Thus, the reaction of platinum(II) sulfoxide-containing complexes with cycloalkenes under photoirradiation occurs by a dissociative mechanism in contrast to the dark process where an associative mechanism is observed: a slow initial stage is the alkene coordination in “the fifth site” of platinum (complex **F**), is followed by intramolecular recoordination {for example, in the case of transformations of alkenes catalyzed by platinum(II) complexes [7]}.

The optimal irradiation time at 20–50°C is 40–50 min (quartz); the subsequent prolonged photolysis only slightly affects the observed change in the rotation angle of the reaction mixture (Fig. 2, curve *1*) and, correspondingly, the reaction rate. The increase in temperature over 40°C under continuous irradiation additionally causes the formation of colloidal platinum owing to decomposition of the metal complex. When the irradiation time is decreased (20 min), with the subsequent keeping in the dark (Fig. 2, curve *4*), the reaction occurs as an independent two-step process: at a high rate under irradiation and at a low rate (equal to that of the dark process), in its absence. At decreased energy of the luminous flux (Pyrex filter), the metal complex does not decompose, but the reaction rate noticeably decreases (Fig. 2, curve *3*).

The replacement of COD by 1-methylcycloocta-1,5-diene (MeCOD) somewhat decreases the reaction rate under photoirradiation (Fig. 2, curves *1* and *2*) and the yield of the final reaction product, which is probably associated with hindered coordination of MeCOD owing to its steric features (the presence of the methyl group at the coordinating double bond).

The data obtained allow us to recommend photoirradiation as an alternative “mild” procedure for the preparation of platinum(II) cycloalkene complexes from disulfoxide complexes as opposed to the thermal route (for example, the irradiation for 40 min at 20°C followed by the dark reaction affords 98% yield of $[Pt(COD)Cl_2]$ in 5 h, whereas without the preliminary irradiation this takes 22 h at 40°C).

EXPERIMENTAL

The IR spectra were taken on IKS-29 (4000–400 cm^{-1}) and Hitachi FIS-3 (400–100 cm^{-1}) spectrometers in KBr. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-200 instrument with an integrating device at an operating frequency of 200 (^1H) and 50 (^{13}C) MHz in $CDCl_3$ without additional references, using as reference the residual proton signal of the deuterated solvent.

Polarimetric measurements were carried out on a Perkin–Elmer-241MC instrument in temperature-controlled quartz cells of length 10 cm. The concentration of the complexes was varied over the range 1.8×10^{-3}– 10^{-4} M. Methylene chloride was used as a solvent.

Photolysis of complexes was carried out by irradiating their solutions in methylene chloride with light of a DRL-400 medium-pressure mercury–quartz burner directly in a polarimetric cell; light was filtered through Pyrex and a 30-mm layer of water.

In the experiments we used methylene dichloride (Merck), cycloocta-1,5-diene, 1-methylcycloocta-1,5-diene (both chemically pure grade), acetone, and cyclohexane (both analytically pure grade).

(–)-*cis*-Dichlorobis(*S*-methyl *p*-tolyl sulfoxide)-platinum(II) was prepared as described in [5], and *cis*-dichlorobis(diethyl sulfoxide)platinum(II), as described in [8].

Dichloro[1,2:5,6-η^4-(cycloocta-1,5-diene)]platinum(II). (–)-*cis*-$[Pt(Me\text{-}p\text{-}TolSO)_2Cl_2]$ (25.0 mg) and 4.4 ml of 0.1 M cycloocta-1,5-diene solution in methylene chloride were mixed, and the volume was brought to 5 ml. Then the reaction mixture was transferred to a polarimetric cell, irradiated for 41 min, and then kept in the dark for 4 h. The reaction solution was poured into 20 ml of cyclohexane, and the resulting precipitate was filtered off and dried in air. Yield 15.5 mg (93%). The ^1H and ^{13}C NMR spectra agree with the data from [1].

Dichloro[1,2:5,6-η^4-(1-methylcycloocta-1,5-diene)]platinum(II). A 37.1-mg portion of *cis*-$[Pt(Et_2SO)_2Cl_2]$ was dissolved in 7 ml of methylene chloride in a quartz flask, 0.1 ml of 1-methylcycloocta-1,5-diene was added, and the solution was irradiated for 1.5 h and then allowed to stand for 2 h. The resulting solution was evaporated to dryness in an air stream, and the solid residue was recrystallized from an acetone—cyclohexane mixture (10 : 1 by volume). The resulting precipitate was dried at 70°C. Yield of the colorless complex 20 mg (66%). IR spectrum, ν, cm^{-1}: 3395–3375, 2950–2870 [ν(CH)]; 1510, 1480 [ν(C=C)]; 1430, 1405, 1370, 1335, 1315, 1238, 1190, 1172, 1100, 1062 [δ(CH, Me)]; 1041, 1025, 1008 [δ(CH, COD)]; 967, 903 [τ(Me)]; 873, 853, 832, 795, 742, 561, 362 [δ(CH, COD)]; 336, 318, 246 [ν(PtCl)]; 211, 168 [δ(PtCl)]. ^1H NMR spectrum, δ, ppm: 1.94 t (3H, CH_3, J_{PtH} 36 Hz), 2.35 m (4H, CH_2, J_{PtH} 67 Hz), 2.70 m (4H, CH_2, J_{PtH} 55 Hz), 5.51 m (3H, CH, J_{PtH} 88 Hz). ^{13}C NMR spectrum, δ_C, ppm: 28.9 t (1C, CH_3, J_{PtC} 29 Hz), 29.3 s (1C, CH_2), 30.6 s (1C, CH_2), 31.5 s (1C, CH_2), 37.9 s (1C, CH_2), 96.1 t (1C, CH, J_{PtC} 150 Hz), 97.8 t (1C, CH, J_{PtC} 152 Hz), 99.9 t (1C, CH, J_{PtC} 164 Hz), 124.0 t (1C, CH, J_{PtC} 126 Hz).

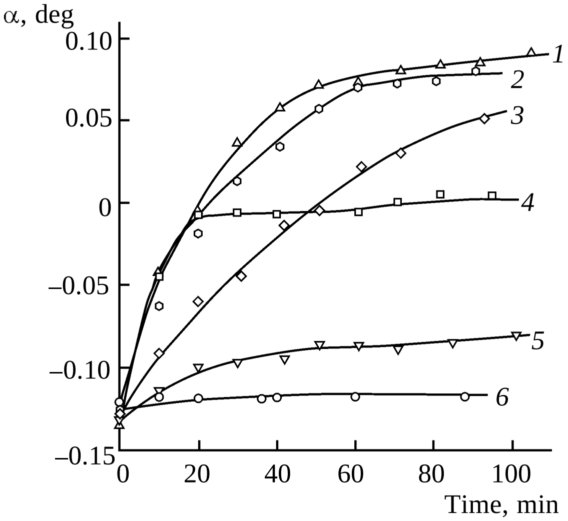


Fig. 2. Variation with time of the observed rotation angle of the chiral composition (α) in methylene dichloride under continuous irradiation of (–)-*cis*-$[Pt(Me\text{-}p\text{-}TolSO)_2\cdot Cl_2]$ in the presence of cycloalkene (molar ratio 1 : 10, 40°C, c_C 1.6×10^{-3} M). (*1, 3, 4, 6*) COD, (*2*) MeCOD, and (*5*) without cycloalkene; (*1, 2, 4*) irradiation for 20 min; (*5*) quartz, (*3*) Pyrex, and (*6*) no irradiation.

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