

## PHOTOINDUCED REACTIONS OF ORGANIC COMPOUNDS WITH TRANSITION-METAL COMPLEXES.

VI.† REDUCTION OF THE  $\text{PtCl}_6^{2-}$  ION WITH CARBON MONOXIDE UNDER THE ACTION OF LIGHT

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We showed recently that the  $\text{PtCl}_6^{2-}$  ion reacts under the action of light with various organic compounds (arenes, olefins, hexane, acetone, and alkyl derivatives of tin and germanium), and as products  $\sigma$ - or  $\pi$ -organometallic complexes of Pt(IV) or Pt(II) are formed [1, 2]. In the present work we extended the range of organic substrates for these reactions, investigating the reaction of the  $\text{PtCl}_6^{2-}$  ion with carbon monoxide.

The thermal reaction of CO with  $\text{PtX}_6^{2-}$  ions ( $X = \text{Cl}, \text{Br}, \text{I}$ ) has been studied in fair detail (see [3] and references in that book). It was found that the reaction rate changes as X changes in the order  $\text{I} > \text{Br} > \text{Cl}$  and depends on the character of the medium. Reaction with  $\text{PtCl}_6^{2-}$  goes at an appreciable rate at  $\sim 80^\circ\text{C}$  and is accelerated by additions of Pt(II); in absence of added Pt(II) the absorption of CO goes with a considerable period of induction.

We investigated the influence of light on the reduction of the  $\text{PtCl}_6^{2-}$  ion in a medium of  $\text{CH}_3\text{COOH}$  with carbon monoxide at a CO pressure of 1 atm at  $15^\circ\text{C}$ . The progress of the reaction was followed from the fall in the absorption of the  $\text{PtCl}_6^{2-}$  ion in the electronic spectrum. In the dark reduction does not occur (Fig. 1). Exposure in a glass vessel ( $\lambda > 320 \text{ nm}$ ) to the full radiation of a high-pressure mercury lamp leads to a rapid fall in the concentration of  $\text{H}_2\text{PtCl}_6$ . No induction period is observed. It is interesting that with decrease in the initial concentration of the  $\text{PtCl}_6^{2-}$  ion the conversion  $\alpha = \{[\text{Pt(IV)}]_0 - [\text{Pt(IV)}]\} / [\text{Pt(IV)}]_0$ , expressed in %, attained during the first 10 min of irradiation rises. The initial reaction rate depends nonlinearly on the intensity of the light. Thus, whereas on exposure to the full radiation of the mercury lamp the concentration of  $\text{PtCl}_6^{2-}$  falls by 63% during the first 10 min, when the intensity of the light is reduced by means of absorbing screens to 70% and to 40% of the full intensity the concentration falls in the same time only by 15 and 7% respectively. The addition of LiCl to the solution lowers the rate of photoreduction somewhat.

The photoreduction of the  $\text{PtCl}_6^{2-}$  ion with carbon monoxide leads to the formation of the carbonylchloro-Pt(II) complex  $[\text{PtCl}_5\text{CO}]^-$ . This complex was obtained as its salt with Cs: a yellow powder which instantaneously yields metallic platinum on the addition of water. The IR spectrum of the salt in mineral oil (intense bands at 2115 and  $2065 \text{ cm}^{-1}$ ) practically coincides with the spectrum of  $\text{Cs}[\text{PtCl}_5\text{CO}]$  prepared by other methods [4, 5].

The irradiation at 77K of a frozen solution of  $\text{H}_2\text{PtCl}_6$  in  $\text{CH}_3\text{COOH}$  saturated with carbon monoxide leads to the appearance in the ESR spectrum of this solution of a signal with  $g = 2.4$ , characteristic for paramagnetic Pt(III) complexes [6, 7]. In absence of CO no signals were observed in this region after photolysis.

As regards the mechanism of the photoreduction of  $\text{PtCl}_6^{2-}$  with carbon monoxide we may suppose that the first stage of the reaction consists in the formation of the excited species  $[\text{PtCl}_6^{2-}]^*$  [6, 7]. There may then occur the homolysis of the Pt-Cl bond with the formation of a Pt(III) derivative and the radical  $\text{Cl}^\cdot$ . Both of these species are probably able to react with the CO molecule, oxidizing it. Also, the Pt(III) complex is able to dispropor-

†For V see [1].

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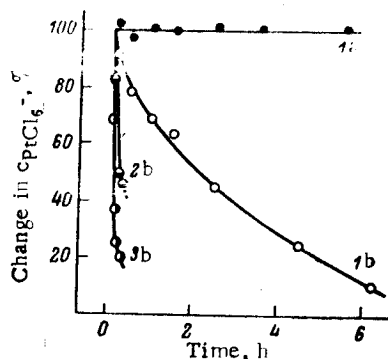


Fig. 1. Kinetic curves of the fall in  $\text{PtCl}_6^{2-}$  concentration in the reaction with CO. Initial  $\text{PtCl}_6^{2-}$  concentrations (M): 1) 0.05; 2) 0.02; 3) 0.01. a) In absence of light at  $15^\circ\text{C}$ ; b) with irradiation at  $15^\circ\text{C}$ .

tionate into Pt(II) and Pt(IV) derivatives. The Pt(II) complex formed in one or another way coordinates CO with the formation of  $[\text{PtCl}_3\text{CO}]^-$ . It should be noted that the formation of Pt(III) complexes in the interaction of Pt(IV) and Pt(II) explains the catalytic action of Pt(II) in the thermal reduction of  $\text{PtX}_6^{2-}$  by carbon monoxide [3, 8].

Hence, the photochemical method found by us for the reduction of the  $\text{PtCl}_6^{2-}$  ion with carbon monoxide under mild conditions in an acid medium provides a convenient preparative method of obtaining the carbonylchloro-Pt(II) complex.

#### EXPERIMENTAL

The irradiation was conducted with the full radiation of a DRSh-1000 high-pressure mercury lamp (1000 W). The concentration of  $\text{PtCl}_6^{2-}$  was determined spectrophotometrically (Specord UV-Vis) from the absorption at 465 nm. The absorption of  $\text{PtCl}_3\text{CO}^-$  in this region can be neglected [3]. The ESR spectra were determined on an ÉPR-20 3-cm range spectrometer (constructed at the Institute of Chemical Physics of the Academy of Sciences of the USSR).

All the experiments were conducted in a glass cylindrical vessel contained in a glass jacket cooled with flowing water. Carbon monoxide was passed into the reaction solution through a capillary with vigorous agitation with a magnetic stirrer.

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#### CONCLUSIONS

Radiation greatly increases the rate of the reduction of the  $\text{PtCl}_6^{2-}$  ion by carbon monoxide in acetic acid.

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