

PHOTOINDUCED REACTIONS OF ORGANIC COMPOUNDS

WITH COMPLEXES OF TRANSITION METALS

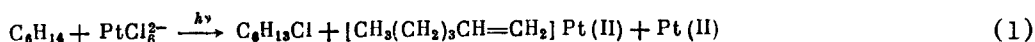
IX.\* OXIDATION OF HEXANE AND OTHER ALKANES AND ISOMERIZATION OF 2-HEXENE UNDER THE INFLUENCE OF THE  $\text{PtCl}_6^{2-}$  ION IN  $\text{CH}_3\text{COOH}$

G. B. Shul'pin, G. V. Nizova, and Yu. V. Geletii

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It was recently found that a  $\pi$ -olefin complex of 1-hexene with Pt(II), which was isolated in the form of an adduct with pyridine (py), viz.,  $[\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}_2]\text{PtCl}_2\text{py}$ , is formed in the irradiation with light with  $\lambda > 300$  nm of a solution of a salt with  $\text{PtCl}_6^{2-}$  and hexane in acetic acid [2, 3] (see also [4]). The complex is also obtained in thermal [5] or  $\gamma$ -induced [6] reactions.

The present research is devoted to a study of the principal products of the photochemical oxidation of hexane by the  $\text{PtCl}_6^{2-}$  ion and to elucidation of the reasons for the formation in this reaction of a  $\pi$  complex of Pt(II) only with 1-hexene. We investigated the accumulation with time of a  $\pi$ -hexene complex of Pt(II), which was isolated by thin-layer chromatography (TLC) on silica gel, and of organic products of oxidation of hexane, which were determined by gas-liquid chromatography (GLC) (see Fig. 1). A mixture of isomeric 1-, 2-, and 3-chlorohexanes (the 2- and 3-chloro isomers could not be isolated by GLC) is virtually the only product of oxidation of hexane that passes into hexane solution during extraction. The corresponding alcohols and ketones were not detected. For all of the samples obtained for various reaction times the sum of the concentrations of the 2- and 3-chloro isomers exceeds the concentration of the 1-chlorohexane formed by a factor of approximately five. With allowance for the number of C-H bonds the selectivity of chlorination of the primary and secondary bonds is  $1^\circ:2^\circ \approx 1:4$ .



It is important that a similar ratio of the isomeric chlorides ( $1^\circ:2^\circ \approx 1:3.5$ ) both in the absence of a solvent and in acetic acid is observed in the photochemically initiated radical-chain chlorination of hexane by molecular chlorine. A study of the compositions of the resulting mixtures of isomeric chlorides in the reaction of  $\text{PtCl}_6^{2-}$  with 2-methylbutane and 2,2,3-trimethylpentane in acetic acid under the influence of light led to the following selectivity ratios:  $1^\circ:2^\circ:3^\circ = 1:4:4$  for isopentane and  $1:3:1.3$  for isoctane. In the case of the photoinitiated chlorination in  $\text{CH}_3\text{COOH}$  by molecular chlorine, in which it is known that attack on the C-H bond is realized by a free chlorine atom, these values

\*See [1] for communication VIII.

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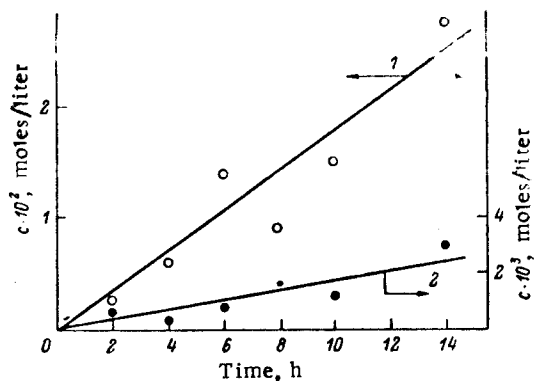
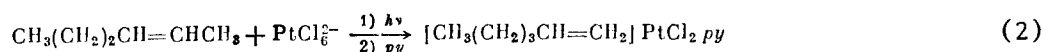


Fig. 1. Kinetics of the accumulation of chlorohexanes (1) and the  $\pi$ -hexene complex of Pt(II) (2) in the photochemical reaction of  $\text{H}_2\text{PtCl}_6$  (0.0386 mole/liter) and hexane (0.6 mole/liter) in  $\text{CH}_3\text{COOH}$ .

are 1:4:4 and 1:3:1, respectively. Let us note that the selectivity of chlorination by molecular chlorine does not change when  $\text{H}_2\text{PtCl}_6$  is introduced into the solution (the exposure time in these experiments was substantially shorter).

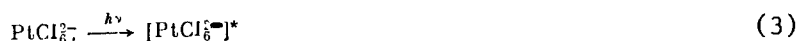
It follows from Fig. 1 that the accumulation of the  $\pi$ -olefin complex and the isomeric chlorohexanes proceeds linearly in the initial section and that the amount of chlorohexane formed exceeds the amount of the  $\pi$  complex by a factor of about 10. There is no appreciable induction period on the kinetic curve of the accumulation of the  $\pi$  complex. Thus it may be concluded that the  $\pi$  complex is not formed from chlorohexane or other relatively stable products of oxidation of hexane.

Additional experiments with olefins were carried out to ascertain the reasons for the formation in this reaction of a  $\pi$  complex of hexene only with a terminal location of the double bond. It has been previously shown that the irradiation of solutions of  $\text{PtCl}_6^{2-}$  or  $\text{PtCl}_4^{2-}$  and olefins with a terminal location of the double bond leads to the rapid formation of  $\pi$ -olefin complexes of Pt(II) [1, 7, 8]. Migration of the double bond was not observed in these processes. Since the formation in the reaction with hexane of a  $\pi$  complex of an olefin only with a terminal location of the double bond may be due to the impossibility of the formation of complexes with olefins that contain an "inner" double bond, we attempted to obtain  $\pi$  complexes with such nonterminal olefins directly in the photochemical reaction of olefins with the  $\text{PtCl}_6^{2-}$  ion. It was found that the irradiation of a solution of 2-hexene and  $\text{PtCl}_6^{2-}$  in acetone leads to the formation of a complex of Pt(II) with 1-hexene, which was previously obtained in a similar reaction with 1-hexene (as monitored by PMR spectroscopy) [5].



We used stilbene as an olefin that contains an "inner" double bond and is not capable of skeletal isomerization. We found that the irradiation of  $\text{PtCl}_6^{2-}$  or  $\text{PtCl}_4^{2-}$  with both the trans and cis isomers of stilbene does not lead to the formation of a  $\pi$ -olefin complex of Pt(II). However, a complex is formed in the thermal reaction of stilbene with  $\text{PtCl}_6^{2-}$ ; the stilbene in the complex has a trans configuration, even if cis-stilbene was subjected to the reaction. Thus the production in reaction (1) of a  $\pi$  complex of Pt(II) only with a terminal olefin cannot constitute evidence that olefins with "inner" double bonds are not formed in this reaction, since the bonds may migrate in the case of coordination with Pt(II) [reaction (2)].

The mechanism of the photochemical reaction of hexane with  $\text{PtCl}_6^{2-}$  is represented as follows. Photoexcitation of the  $\text{PtCl}_6^{2-}$  ion leads to homolysis of the Pt-Cl bond: (3) and (4).



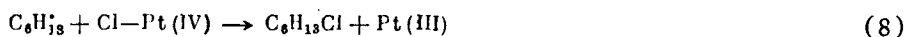
A free chlorine atom, which reacts rapidly with the alkane via reaction (5), is formed as a result.



The alkyl radical then reacts with the strong oxidizing agent Pt(IV) that is present in the system. This reaction evidently proceeds quite rapidly, since no effect of a change in the oxygen concentration on the composition of the products and rate of the reaction can be noted. Oxidation of the radical may lead to the formation of a carbonium ion (6), which then rapidly adds a Cl<sup>-</sup> ion (7).



The possibility that the reaction of the alkyl radical with Pt(IV) proceeds via a mechanism involving detachment of halogen from the metal complex is not excluded; in this case the alkyl chloride is obtained in one step (8).



The Pt(III) complex is unstable and undergoes disproportionation (9).



Two pathways may lead to the  $\pi$ -hexene complex of Pt(II). The first pathway consists in the formation of an olefin (via splitting out of H<sup>+</sup> from the carbonium ion or disproportionation of the alkyl radicals), which is coordinated with the Pt(II) produced in the redox process: (10) and (11).



In addition, recombination of Pt(III) and a hexyl radical may lead to the formation of a  $\sigma$ -hexyl complex of Pt(IV) which, by splitting out of hydrogen from the  $\beta$  position of the alkyl chain, is converted to a  $\pi$ -olefin complex of Pt(II): (12) and (13).



Since [Pt(IV)]  $\gg$  [Pt(III)], process (12) can occur only in a solvent cage. Reaction (12) is modeled by the reaction of the PtCl<sub>6</sub><sup>2-</sup> ion with acetone under the influence of light, which leads to the formation of a  $\sigma$ -acetyl complex of Pt(IV) [2]. In this case signals of a CH<sub>3</sub>COCH<sub>2</sub><sup>\cdot</sup> radical and a paramagnetic Pt(III) complex are observed in the EPR spectrum at 77°K [9]. The formation of  $\pi$ -olefin complexes of Pt(II) in the reaction of Pt(II) with alkyl halides, in which the intermediate development of  $\sigma$ -alkyl complexes of Pt(IV) was rigorously established [2, 10], may serve as a model of process (13). The conversion of these  $\sigma$ -alkyl complexes of Pt(IV) to  $\pi$ -olefin derivatives of Pt(II) is accelerated by irradiation [11].

#### EXPERIMENTAL

The photochemical reactions were carried out at room temperature in a cylindrical glass flask included in a jacket cooled by running water. The solution was stirred vigorously with a magnetic stirrer. In the kinetic experiment reflected in Fig. 1, 10 ml of a solution in acetic acid containing  $3.86 \cdot 10^{-2}$  mole/liter H<sub>2</sub>PtCl<sub>6</sub>, 0.6 mole/liter hexane, and 0.3 ml of water was irradiated with the total light of a DRSh-1000 high-pressure mercury lamp (1000 W) for a certain length of time. A 1-ml sample of a solution of the internal standard (cyclohexyl chloride) in hexane was added to the solution, a small amount of water was added to the resulting mixture, and the hexane layer was separated. The amounts of hexyl chlorides in it were determined by GLC (with a Biokhrom-1 chromatograph with a 4-m long column packed with 5% Silicone-XE 60 on a Chromaton N-AW-DMSC support). The residual aqueous acidic solution was evaporated at reduced pressure, and the residue was extracted with hot chloroform. An aqueous solution of pyridine (0.05 ml in 10 ml of water) was added to the washed (with water) organic extract, and the chloroform extracts were washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated at reduced pressure, and the residue was chromatographed on silica gel plates (with elution by chloroform) with collection of the yellow-green band of the  $\pi$ -hexene complex of Pt(II), the amount of which was determined spectro-

photometrically (with a Specord UV-Vis spectrophotometer) in ethanol solution at  $23,570\text{ cm}^{-1}$ . The photoinitiated chlorination of 2-methylbutane and 2,2,3-trimethylpentane was carried out similarly. The isomeric chlorides of 2-methylpentane was carried out similarly. The isomeric chlorides of 2-methylbutane were analyzed without prior extraction by direct analysis of the reaction solution. The isomeric chlorides of 2,2,3-trimethylpentane were extracted with pentane after irradiation. The photoinitiated chlorination was carried out both without a solvent and in acetic acid solution with slow passage of  $\text{Cl}_2$  through the solution and irradiation of the latter. The degree of chlorination did not exceed 5-10%. The ratio of the concentrations of the isomeric chlorides was determined in all cases as the ratio of the areas of the corresponding peaks. Absolute measurement of the concentrations of the chlorohexanes was made with the use of an internal standard (cyclohexyl chloride). Calibration was carried out by means of artificially prepared solutions of hexyl chlorides and cyclohexyl chloride over the same concentration ranges.

Photochemical Reaction of  $\text{PtCl}_6^{2-}$  with 2-Hexene. A solution of 0.1 g of  $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and 1 ml of 2-hexene in 5 ml of acetone was irradiated in a glass flask at room temperature with the total light of a DRS-1000 lamp for 30 min. The resulting precipitate was removed by filtration, and the acetone was evaporated at reduced pressure. The residue was dissolved in chloroform, and the solution was treated with pyridine as described above to give 0.016 g (10%) of a  $\pi$  complex of Pt(II) with 1-hexene, which was identified by comparison of the  $R_f$  values and the PMR spectra (see [5]).

Photochemical Reaction of  $\text{PtCl}_6^{2-}$  with cis-Stilbene. A solution of 0.1 g of  $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and 0.1 ml of cis-stilbene in 5.5 ml of acetone was irradiated for 3 h. A  $\pi$  complex of stilbene with Pt(II) was not detected.

Thermal Reaction of  $\text{PtCl}_6^{2-}$  with trans-Stilbene. A solution of 0.1 g of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and 0.18 g of trans-stilbene in 15 ml of  $\text{CH}_3\text{COOH}$  was heated at  $70^\circ\text{C}$  for 20 min. The solvent was evaporated at reduced pressure, and the residue was dissolved in chloroform and treated with aqueous pyridine. Chromatography on silica gel gave 0.048 g (22%) of the  $(\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5)\text{-PtCl}_2\text{py}$  complex. In the complex stilbene has the trans configuration, since only trans-stilbene was isolated by the action of excess pyridine on it.

Thermal Reaction of  $\text{PtCl}_6^{2-}$  with cis-Stilbene. Similarly, the reaction of 0.1 g of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and 0.06 g of cis-stilbene in  $\text{CH}_3\text{COOH}$  gave 0.02 g (5.5%) of the  $(\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5)\text{-PtCl}_2\text{py}$  complex, in which stilbene has the trans configuration.

#### CONCLUSIONS

The irradiation with light of a solution of the  $\text{PtCl}_6^{2-}$  ion and hexane in acetic acid leads to the formation of chlorohexane isomers and a  $\pi$  complex of Pt(II) with 1-hexene. The photochemical reaction of  $\text{PtCl}_6^{2-}$  with 2-hexene gives a  $\pi$  complex of Pt(II) with 1-hexene.

Light does not induce the reaction of  $\text{PtCl}_6^{2-}$  with stilbene, whereas thermal reaction with the cis or trans isomer leads to the formation of a  $\pi$  complex of Pt(II) only with trans-stilbene.

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