

PHOTOINDUCED REACTIONS OF ORGANIC COMPOUNDS  
WITH COMPLEXES OF TRANSITION METALS

V.\* FORMATION OF A  $\pi$ -OLEFIN COMPLEX OF Pt(II)  
IN THE REACTION OF HEXANE WITH  $\text{PtCl}_6^{2-}$  IN  $\text{CH}_3\text{COOH}$   
UNDER THE ACTION OF LIGHT

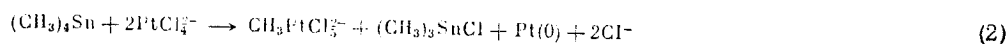
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Processes of the activation of saturated hydrocarbons with complexes of transition metals in solutions have attracted much attention in recent years (see the reviews [2-5]). This problem is of importance both from the theoretical point of view (the chemical inertness of alkanes is well known), and in its practical aspects (the need for a search for fundamentally new ways of processing hydrocarbon raw materials). The first investigation on the activation of alkanes by metal complexes was published in 1969 [6]. This concerned deuterium exchange in methane and other lower alkanes in a medium of deuterium oxide and in presence of Pt(II) salts. Somewhat later it was found that alkanes are oxidized to alkyl chlorides by Pt(IV) compounds, and a Pt(II) complex added to the reaction mixture acts as a catalyst [7]. It is supposed that both H-D exchange and the oxidation of alkanes have a common first stage: the oxidative addition of the hydrocarbon to Pt(II) with the formation of an alkylhydrido-Pt(IV) complex. This stage can be represented formally as follows:



It was shown recently that alkyl iodides [8-10] and  $(\text{CH}_3)_4\text{Sn}$  [11-13] add oxidatively to the complex  $\text{PtCl}_4^{2-}$  at room temperature. In both cases there is formed the monoalkyl complex  $\sigma\text{-AlkPtLCl}_4^{n-}$ , in which  $\text{L}=\text{Cl}$  ( $n=2$ ) or  $\text{L}=\text{H}_2\text{O}$  ( $n=1$ ). It is important to emphasize that the second component of the organic substrate, i.e., the iodine atom or  $\text{Sn}(\text{CH}_3)_3$  group, in the course of the reaction is bound by another species, containing platinum. It is probable that in the case of tetramethylstannane an oxidation-reduction reaction with Pt(II) occurs, leading to the formation of Pt(0) and  $(\text{CH}_3)_3\text{SnCl}$  (2).

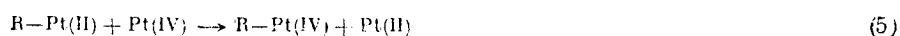


As in the case of the oxidation of alkanes, the  $\text{PtCl}_4^{2-}$  complex accelerates the formation of the  $\sigma$ -methyl complex of platinum (IV) in the thermal reaction of  $\text{PtCl}_6^{2-}$  with  $(\text{CH}_3)_4\text{Sn}$ , which goes at room temperature. On analogy with the reactions of the complex of Pt(II) with trimethylstannane or alkyl iodides it may be supposed that the oxidative addition of an alkane to Pt(II) is not bound to lead to the formation of an intermediate alkylhydrido-Pt(IV) complex. For example, this addition may proceed synchronously with the reductive elimination of HCl, and then the reaction becomes in its result analogous to the electrophilic substitution (3).



It is known that the complex  $\text{PtCl}_4^{2-}$  metalates arenes, probably by an electrophilic-substitution mechanism [14].

The Pt(II) complex obtained in reaction (3) may react with  $\text{D}^+$  or be oxidized into a  $\sigma$ -alkyl Pt(IV) complex [(4), (5)].



\* For preliminary communication see [1]; for IV see [47].

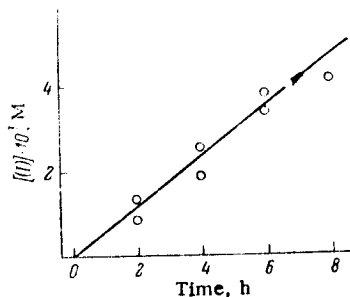


Fig. 1

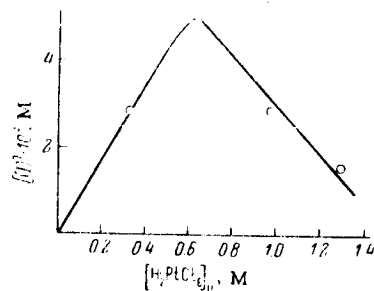
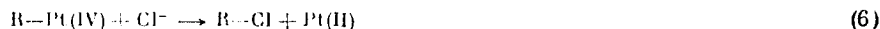


Fig. 2

Fig. 1. Kinetic curve of the accumulation of the complex (I) in the reaction of  $\text{H}_2\text{PtCl}_6$  (initial concentration 0.064 M) with hexane (1.88 M) in  $\text{CH}_3\text{COOH}$  at  $20^\circ\text{C}$  with exposure to the total radiation of a DRSh-1000 high-pressure mercury lamp.

Fig. 2. Relation of the concentration of the complex (I) in the irradiation (8 h,  $20^\circ\text{C}$ ) of a solution of  $\text{H}_2\text{PtCl}_6$  and hexane (1.88 M) in  $\text{CH}_3\text{COOH}$  to the concentration of  $\text{H}_2\text{PtCl}_6$ .

The  $\sigma$ -methyl complex of Pt(IV) is more stable than the analogous methyl derivative of Pt(II), but even it reacts rapidly with  $\text{Cl}^-$  [8, 9] by the scheme (6).



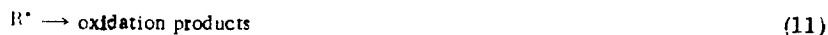
The formation of a  $\sigma$ -methyl Pt(IV) complex in the system  $\text{CH}_4\text{-PtCl}_4^{2-} \text{-PtCl}_6^{2-}$  was recorded by the PMR method [15]. The chloride Pt(II) complex in reaction with alkanes probably behaves as a "soft catalyst" [4], breaking the C-H bond heterolytically. In recent years many examples have become known of the activation of alkanes through the oxidative addition of the alkane to a complex of a transition metal [16-32].



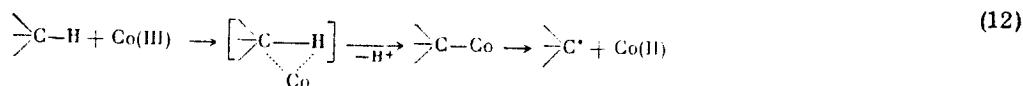
Some such reactions are induced photochemically [26-30], and the role of light probably lies in the elimination of one of the ligands of the complex and the formation of a coordinatively unsaturated species, able to undergo oxidative addition with the alkane (8).



On the other hand, the oxidation is known of alkanes and alkylaromatic hydrocarbons by complexes of Co(III) and Ce(IV) [33-39], which can be classified as "hard acids" in the Pearson terminology. The mechanism of these reactions have not been studied carefully. It has been suggested that the oxidation goes by a mechanism which includes the formation of a radical cation [(9)-(11)].



However, we cannot rule out [4] the possibility also of the formation of the radicals  $\text{R}^{\bullet}$  in the attack by Co(III) on a C-H bond with the intermediate formation of  $\sigma$ -alkyl complexes of Co(III) (12).

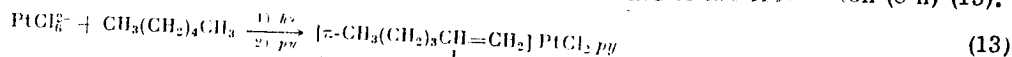


It was recently shown that the oxidation of 1,2-diphenylethane with Ce(IV) nitrate or Co(III) acetate in acetic acid can proceed with the formation of a radical cation only in the case of the first oxidant [39].

It was shown in [40] that, on heating ( $\sim 80^\circ\text{C}$ ), in a  $\text{CF}_3\text{COOH-H}_2\text{O}$  mixture hexane reacts with  $\text{H}_2\text{PtCl}_6$ , i.e., with the complex of a metal in a high degree of oxidation, in the course of a few hours with the formation

mainly of 1-chlorohexane. Moreover, in this reaction there is also obtained a small amount of Pt(II) with  $\pi$ -hexene, and this was isolated in the form of  $(C_6H_{12})PtCl_2py$  and identified by PMR [41]. It was suggested [41] that the formation of the  $\pi$  complex proceeds through an intermediate Pt(IV) complex of Pt(IV).

In this communication we describe the results of an investigation of the reaction of  $PtCl_6^{2-}$  ion with hexane induced by radiation. In the irradiation of a homogeneous solution of  $H_2PtCl_6$  and hexane in acetic acid at room temperature with the total radiation of a DRSh-1000 high-pressure mercury lamp the formation of a  $\pi$ -hexene complex of Pt(II) is observed. The complex was isolated in the form of an adduct of  $\pi$ -hexene with pyridine and purified by means of TLC on silica gel. As in the case of the thermal reaction [41], it was shown by means of PMR that only the complex of Pt(II) with 1-hexene is formed. The kinetic curve for the formation of the  $\pi$  complex is shown in Fig. 1. The relation obtained is linear throughout the whole time of the irradiation (8 h) (13).



The initial reaction rate (concentration of complex after 4 h of irradiation) rises linearly with rise in the hexane concentration (for  $[PtCl_6^{2-}]_0 = 0.039$  M, after 4 h of irradiation):

$[C_6H_{14}]_0, M$	0.75	1.5	1.9
$[I] \cdot 10^8, M$	2.0	2.7	4.3

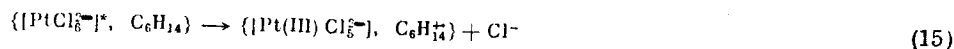
The reaction is therefore of first order with respect to the hydrocarbon. We also investigated the relation of the rate  $W$  of reaction (13) (concentration of the  $\pi$  complex formed after 8 h of irradiation) to the initial concentration of  $PtCl_6^{2-}$  (Fig. 2). Whereas in the range  $(0-6) \cdot 10^{-2}$  M  $PtCl_6^{2-}$  the reaction rate rises in proportion to  $[PtCl_6^{2-}]_0$  (first order), after that there is a marked slowing of the reaction as  $[PtCl_6^{2-}]$  rises. Under the conditions of the experiment, at a concentration of  $PtCl_6^{2-}$  of 0.06 M the solution becomes opaque for the light of the mercury lamp [42]. However, this effect should only lead to a limit to the region in which  $W$  depends on  $[H_2PtCl_6]$  and should not act as the cause of a fall in the reaction rate. The observed fall in  $W$  probably indicates that the  $\pi$  complex formed enters into further reactions. In the present work we confine ourselves to an analysis of the accumulation of the  $\pi$ -hexene complex. The effective rate constant for the formation of the  $\pi$  complex, calculated from the relations of its yield to the time and the initial concentrations of  $PtCl_6^{2-}$  and hexane, is  $2.4 \cdot 10^{-6}$  liter  $\cdot$  mole $^{-1}$  sec $^{-1}$  ( $\pm 50\%$ ).

In discussing the mechanism of the formation of the  $\pi$  complex (I) in reaction (13) we must take account of the known fact of the excitation of the species  $PtCl_6^{2-}$  under the action of light ( $\lambda$  365 nm) [43-45] (14).

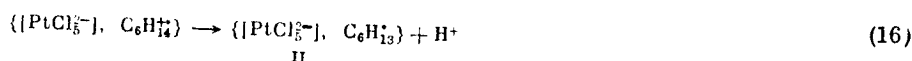


As was shown in [42] for the case of the reaction of the complex of Pt(IV) with arenes, the structure of the excited species active in the reaction can be represented as a charge-transfer complex  $[Pt(III)Cl_5Cl]^*2^-$ .

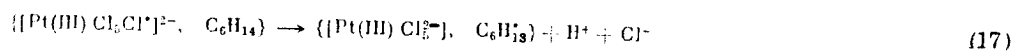
An analogous description of the photoexcited complex  $IrCl_6^{2-}$  is given in [46]. It may be supposed that the process of the formation of the  $\pi$ -hexene complex occurs without the free radicals escaping into the body of the solution. At relatively high concentrations of hexane in the solution, such as were used in the experiments, there is one or several hexane molecules close to each  $PtCl_6^{2-}$  species. It is possible that the primary act in the interaction of hexane with the active excited species  $[Pt(III)Cl_5Cl]^*2^-$  is the transfer of an electron from the alkane to the complex, proceeding in a solvent cage, which is analogous to the situation postulated in reactions of the complex  $IrCl_6^{2-}$  with arenes, olefins, and acetone [42, 47, 48]. Here we must have the formation of a pair consisting of the radical cation and a Pt(III) complex. This process is probably accompanied by the elimination of the  $Cl^-$  ion (15).



The radical cation of hexane is unstable and passes into a hexyl radical with the loss of a proton (16).

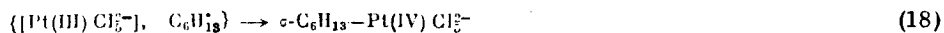


The formation of the pair (II) may arise also in the reaction of the hexane molecule with the  $Cl^{\bullet}$  radical in a cage with the simultaneous formation of HCl (17).



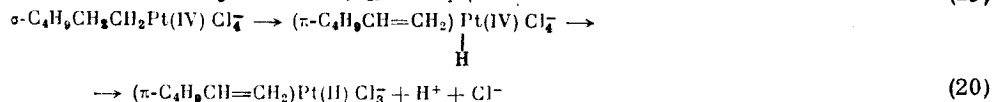
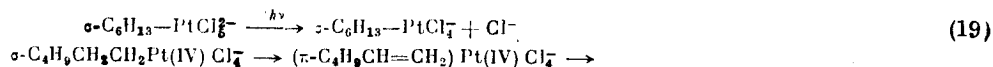
As a result, the irradiation leads to the formation of an alkyl radical and a Pt(III) complex in a solvent cage. It should be noted that in the irradiation of frozen solution of  $\text{PtCl}_6^{2-}$  in methanol [43] or acetone [48] or in acetic acid in presence of arenes [49] or olefins [50] it is possible to establish the formation, by means of the ESR spectra, of both organic radicals and paramagnetic Pt(III) complexes. The irradiation of a frozen solution of  $\text{H}_2\text{PtCl}_6$  and hexane in  $\text{CH}_3\text{COOH}$  at 77 K does not lead to the formation of ESR signals, which is possibly to be explained by too low a concentration of paramagnetic species in this case.

We can envisage several courses along which the further transformation of the two radical species may go. The recombination of the species in a solvate cage gives the  $\sigma$ -alkyl Pt(IV) complex (18).



Analogous stages were postulated for a number of reactions of the complex  $\text{PtCl}_6^{2-}$  with organic compounds. Thus, the formation of stable  $\sigma$ -alkyl Pt(IV) complexes in photoinduced reactions of  $\text{PtCl}_6^{2-}$  with acetone and tetramethylstannane probably proceeds with the recombination of  $\text{Pt(III)Cl}_5^{2-}$  with the radicals  $\text{CH}_3\text{COCH}_2^\bullet$  or  $\text{CH}_3^\bullet$  [48, 13]. The recombination of  $\text{PtCl}_5^{2-}$  and an arene radical cation gives Wheland's complex, which after the loss of a proton forms a  $\sigma$ -aryl Pt(IV) complex [42, 49].

The  $\sigma$ -hexyl complex of Pt(IV) is unstable, and, losing hydrogen from the  $\beta$  position of the alkyl chain, it is converted into the  $\pi$ -hexyl complex of Pt(II). It is possible that light accelerates this reaction, conducting to the initial elimination of a chloride ion from the coordination sphere of platinum [(19) and (20)].



Confirmation of this scheme may be provided by experiments with the  $\sigma$ -ethyl complex of Pt(IV) prepared by the oxidative addition of  $\text{C}_2\text{H}_5\text{I}$  to  $\text{PtCl}_4^{2-}$  [9]. It can be observed directly that under the action of light this complex is converted into the  $\pi$ -ethylene complex of Pt(II), identified by means of PMR. Apart from this, the irradiation of solutions of  $\text{PtCl}_6^{2-}$  with  $(\text{C}_2\text{H}_5)_4\text{Ge}$  or  $(\text{C}_2\text{H}_5)_2\text{Sn}(\text{CH}_3)_2$  in  $\text{CH}_3\text{COOH}$  also leads to the formation of the  $\pi$ -ethylene complex of Pt(II), and in the last case by means of PMR the intermediate  $\sigma$ -ethyl complex of Pt(IV) was also recorded [13].

Another possible way in which the  $\pi$ -hexane complex of Pt(II) may be formed is as follows. It is probable that, as well as the recombination of the paramagnetic species in the pair (II) in accordance with reaction (18), an oxidation-reduction process may occur with the formation of a Pt(II) complex and carbocation (21).



The unstable carbocation  $\text{C}_6\text{H}_{13}^+$  is converted into hexene with the elimination of a proton by reaction (22).



As shown in [47, 50], under the action of light the molecule of the olefin readily reacts with the Pt(II) or Pt(IV) complex, resulting in the formation of the  $\pi$ -hexene complex of Pt(II).

We may envisage other routes to the formation of hexene with the participation of the radicals  $\text{Cl}^\bullet$  or  $\text{C}_6\text{H}_{13}^\bullet$ . The first species may be formed in the photolysis of the Pt-Cl bond [43, 45], and the second in the reaction of  $\text{Cl}^\bullet$  with the hexane molecule or as a result of the decomposition of the pair (II). However, in this case it would be expected that, not only 1-hexene, but also other hexene isomers would appear. On the other hand, we cannot rule out the possibility that only 1-hexene is capable of forming a  $\pi$ -olefin complex of Pt(II) under the action of light (e.g., 2- and 3-hexenes give  $\pi$ -allyl complexes).

In this connection it should be noted that the addition to the reaction mixture of even small amounts ( $\sim 10^{-2}$  M) of NaCl leads to a sharp fall in the yield of the  $\pi$ -hexene complex (measured after 8 h of irradiation), and in this case the results of the experiments cease to be quantitatively reproducible. Simultaneously we observe the formation of considerable amounts ( $\geq 0.1$  M) of the  $\text{PtCl}_4^{2-}$  ion, the concentration of which rises as the irradiation time increases. It is possible that these features arise from the radical character of the processes occurring in presence of chloride ions. It may be supposed that the  $\text{Cl}^-$  ion plays the role of a catalyst, stabilizing the chlorine radical formed in the body of the solution in the photolysis of the Pt-Cl bond.

The formation of  $\text{Cl}_2^{\cdot+}$  species can be observed directly by the ESR method: in the photolysis of frozen solutions of  $\text{PtCl}_6^{2-}$  in presence of large amounts of  $\text{LiCl}$  [51]. In solution the chlorine radical anion chlorinates hexane, while the  $\text{PtCl}_5^{2-}$  complexes disproportionate into  $\text{PtCl}_4^{2-}$  and  $\text{PtCl}_6^{2-}$ .

It is noteworthy that, when in photochemical reaction with hexane some batches of commercial reagent  $\text{H}_2\text{PtCl}_6$  containing, in particular, paramagnetic complexes as impurities, we again observe the rapid formation of  $\text{PtCl}_4^{2-}$  and quantitatively nonreproducible results. It is probable that, in this case also, the cause of such behavior in the system is the occurrence of free-radical processes.

In conclusion we may point out that the reaction of the  $\text{PtCl}_6^{2-}$  ion with hexane in acetic acid, leading to the formation of the Pt(II)  $\pi$ -hexene complex, is induced not only by light, but also by  $\gamma$  radiation [52]. The concentration of the complex (I) rises linearly with increase in the dose of radiation and attains 16.5% (calculated on the Pt) at a dose of 132 Mrad. At a very high dose (300 Mrad) all the  $\text{H}_2\text{PtCl}_6$  taken undergoes transformation, but in this case in the isolation of the complex by chromatography on silica gel we observe its decomposition with the formation of metallic platinum. It is probable that at doses of radiation that are not too high reaction induced by  $\gamma$  radiation has the same mechanism as in the photochemical reaction and starts with the excitation of the  $\text{PtCl}_6^{2-}$  ion under the action of  $\gamma$  quanta.

### EXPERIMENTAL

The reactions were conducted at room temperature in a cylindrical quartz vessel enclosed in a jacket for water cooling. During the process the solution was agitated vigorously with a magnetic stirrer. At the end of the irradiation the solution was vacuum-evaporated at room temperature. The residue obtained was extracted with chloroform, and the extract was shaken with aqueous pyridine (0.05 ml of pyridine in 10 ml of water), washed with water, and dried with  $\text{Na}_2\text{SO}_4$ . Chloroform was vacuum-evaporated, and the residue was applied to a plate carrying silica gel. As eluent we used chloroform. We collected a lemon-yellow band of complex, the amount of which was determined spectrophotometrically from its absorption in the visible region of the spectrum (Specord UV-Vis spectrophotometer, frequency  $23570 \text{ cm}^{-1}$ , solutions in ethanol).

We thank A. E. Shilov for his interest in the work and for useful discussions.

### CONCLUSIONS

1. The irradiation of a solution of a salt with a  $\text{PtCl}_6^{2-}$  anion and hexane in  $\text{CH}_3\text{COOH}$  leads to the formation of a  $\pi$ -hexene complex of Pt(II) in yields of up to 10%.
2. The  $\pi$ -olefin complex is formed probably as a result of the  $\beta$  elimination of hydrogen from the alkyl chain of the intermediately formed  $\sigma$ -hexyl complex of Pt(IV) or as a result of the oxidation of the intermediate hexyl radicals to carbocations with the subsequent coordination of the hexene formed with Pt(II).

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