

PHOTOINDUCED REACTIONS OF ORGANIC COMPOUNDS WITH TRANSITION METAL COMPLEXES.
COMMUNICATION 1. FIRST EXAMPLE OF SUBSTITUTION IN THE AROMATIC NUCLEUS IN
PHOTOEXCITATION OF AN ELECTROPHILIC REAGENT: FORMATION OF σ -ARYL COMPLEXES
OF Pt(IV) IN THE REACTION OF $PtCl_6^{2-}$ WITH ARENES

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Electrophilic substitution in aromatic compounds, conducted in thermal conditions, has long been known, and its mechanism has been studied in detail [1]. However, reactions with excitation of the electrophile by light have not yet been described. The absence of examples of such photoinduced reactions could be due to a number of causes. First, the reaction must take place very slowly at $\sim 20^\circ C$ in the dark so that the reaction of the arene with the electrophile would only be induced by the effect of light. Second, only the electrophilic reagent should selectively go into an excited reactive state on irradiation. Finally, irradiation should not cleave the aryl-electrophile bond in the product formed. It is clear that all of these requirements are not satisfied by the systems known in ordinary electrophilic substitution (nitration, sulfonation, mercuration, etc.). In some photoinduced reactions of arenes (deuterium exchange [2-4], Friedel-Crafts acylation [5]), the light causes excitation of the arene, which then reacts with the electrophile.

The first example of electrophilic substitution (metallization) in arenes induced by photoexcitation of an electrophilic reagent [6] was discovered on the example of the reaction of $PtCl_6^{2-}$ and an arene (ArH) in CH_3COOH or $CF_3COOH-H_2O$, resulting in the σ -aryl derivative of Pt(IV), isolated as the $[ArPtCl_4NH_3]NH_4$ salt. These complexes were also synthesized in the reaction of $PtCl_6^{2-}$ and ArH in a solution of an organic acid at $70-100^\circ C$ [7-9]. The kinetics and some features of the thermal reaction have been studied [10-12]. A detailed description of the photoinduced reaction is presented in the present article.

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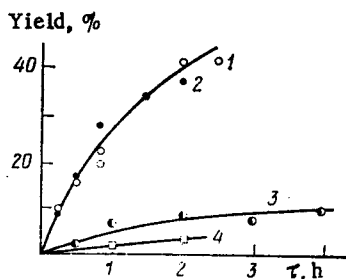


Fig. 1. Kinetic curves of the accumulation of σ -aryl complexes of Pt(IV) (I) in reaction (1): 1) anisole in $\text{CH}_3\text{COOH-H}_2\text{O}$ (90:1); 2) anisole in $\text{CF}_3\text{COOH-H}_2\text{O}$ (4:1); 3) toluene in $\text{CH}_3\text{COOH-H}_2\text{O}$ (90:1); 4) toluene- d_8 in $\text{CH}_3\text{COOH-H}_2\text{O}$ (90:1). Irradiation with light from a DRSh-1000 lamp with a FS-1 filter (322-485 nm) at 22°C. Starting concentration of $[\text{H}_2\text{PtCl}_6]_0 = 0.08 \text{ M}$.

EXPERIMENTAL

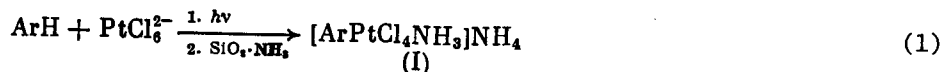
All of the experiments were conducted in air in a cylindrical quartz vessel 2 cm in diameter with illumination by the total light from a DRSh-1000 high-pressure mercury lamp and stirring (the distance to the light source was 20 cm). In the kinetic experiments, the solution was extracted a fixed time after the reaction ended to eliminate the arene, CHCl_3 after addition of a small amount of water, vacuum evaporated below 40°C, and the residue was chromatographed on silica gel containing NH_3 . (NH_3 -silica gel was prepared by holding silica gel in a dessiccator above an aqueous solution of NH_3 .) An acetone-hexane mixture (2:1) eluted the Pt(IV) σ -aryl complex, and the amount was determined spectrophotometrically on a Specord UV-VIS. The EPR spectra were made on an EPR-20 three-centimeter range spectrometer from the Institute of Chemical Physics, Academy of Sciences of the USSR. The PMR spectra were recorded on Bruker SXP-4-100 (90 MHz) and Bruker SXP-300 (300 MHz) spectrometers.

Reaction of PtCl_6^{2-} with Anisole. A solution of 0.2 g of $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 2 ml of anisole in 18 ml of CH_3COOH was irradiated for 2 h at 17°C. Then 10 ml of water were added to the solution and it was extracted with CHCl_3 three times. The solvent was evaporated at low pressure, and the residue in acetone solution was transferred to the NH_3 -silica gel column treated with hexane. An acetone-hexane mixture (2:1) eluted the yellow-orange band of the $[\text{CH}_3\text{OC}_6\text{H}_4\text{PtCl}_4\text{NH}_3]\text{NH}_4$ complex. The complex was additionally purified on silica gel plates. The yield was 0.074 g (44%).

The other syntheses were conducted in the same way.

DISCUSSION OF RESULTS

The photoinduced reaction of the PtCl_6^{2-} ion with the arenes (1) took place in irradiation of a solution of the reagents in CH_3COOH or the $\text{CF}_3\text{COOH-H}_2\text{O}$ mixture during several hours with the total light from a high-pressure mercury lamp with fundamental irradiation maxima at 365, 405, and 436 nm



The yields of the Pt(IV) σ -aryl complexes formed were 10-45% (Table 1). A σ -aryl complex of anisole (A) and Pt(IV) was also obtained in irradiation of a solution of the reagents in acetone, but the yield was insignificant, and a σ -acetyl complex of Pt(IV) was primarily formed [6].

The rate of formation of the complex of Pt(IV) with A (Fig. 1) was not dependent on the solvent. In the reaction of toluene with PtCl_6^{2-} , an H/D isotopic effect of the reaction (2) was found.

The yield of the complex in the reaction of PtCl_6^{2-} with anisole was weakly dependent on the concentration of anisole used in excess. With an increase in the A/ PtCl_6^{2-} molar ratio from 7 to 40, the yield of (I) increased from 16 to 26% ($[\text{Pt(IV)}]_0 = 7.7 \cdot 10^{-2} \text{ M}$, 50 min, 22°C). The amount of complex (I) formed in reaction (1) with A initially increased with an increase in the starting concentration of PtCl_6^{2-} , and then almost stopped being dependent on $[\text{PtCl}_6^{2-}]_0$. The relative yield of the σ -complex monotonically decreased with an increase in $[\text{PtCl}_6^{2-}]_0$. The yield of complex (I) in the case of A also decreased slightly when LiCl was added to the reaction mixture (for $[\text{PtCl}_6^{2-}]_0 = 7.7 \cdot 10^{-2} \text{ M}$, the yield of (I) decreased from 28% after 50 min in $\text{CF}_3\text{COOH-H}_2\text{O}$ with $[\text{LiCl}] = 0$ to 12% with $[\text{LiCl}] = 0.31 \text{ M}$) or an oxidant (SeO_2). The addition of Na_2PtCl_4 to the system also resulted in a decrease in the rate of accumulation of (I). The change in the initial yield of (I) for A in the 21-56.5°C range corresponded to the activation energy of reaction (1) of $E_a = 5 \pm 1 \text{ kcal/mole}$. We note that the observed activation energy is significantly higher for the thermal reaction with arenes. $E_a = 25-30$

TABLE 1. Photoinduced Metallization of Aromatic Compounds by PtCl_6^{2-} Ion in Protic Media*

Initial complex	Arene	Solvent†	Reaction time, h	Yield of complex (I), %
$\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	Toluene	$\text{CH}_3\text{COOH}-\text{H}_2\text{O}$ (30:1)	2.3	11
$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	Toluene	$\text{CF}_3\text{COOH}-\text{H}_2\text{O}$ (5:1)	2	10
$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	Ethylbenzene	$\text{CH}_3\text{COOH}-\text{H}_2\text{O}$ (90:1)	1	11
$\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	Anisole	$\text{CH}_3\text{COOH}-\text{H}_2\text{O}$ (90:1)	2	44
$\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	Anisole	$\text{CF}_3\text{COOH}-\text{H}_2\text{O}$ (5:1)	1.5	41
$\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	Phenol	$\text{CH}_3\text{COOH}-\text{H}_2\text{O}$ (30:1)	0.5	28
$\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	Phenol	H_2O	1	9
$\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	Naphthalene	$\text{CH}_3\text{COOH}-\text{H}_2\text{O}$ (90:1)	1.5	16

*Irradiation in a quartz vessel with the total light from a DRSh-1000 lamp at 20°C. Starting concentration of PtCl_6^{2-} of 0.08 M.

†The volume ratios are indicated in parentheses.

kcal/mole for toluene [12]. Irradiation with networks with a different transmitting capacity showed that a decrease in the intensity of the incident light from the DRSh-1000 lamp to 25% did not result in a marked decrease in the rate of the reaction, and the yield of (I) only decreased directly proportionally to the value of the intensity with a further decrease in the intensity of the light.

In contrast to the similar thermal reaction [12], the formation of only (>95%) the p-metallized isomer from monosubstituted benzene and the absence of p-m isomerization was characteristic of photochemical reaction (1) (in the thermal reaction, approximately 10% m-isomer of the σ -tolyl complex is initially formed, and its concentration increases to 65% after several hours at 70-90°C [12]).

The relative rates of metallization of the different arenes in reaction (1) were determined by the method of competitive reactions [11]: phenol 8, anisole 4, phenetole 4, diphenyl oxide 1.9, toluene 1. The logarithms of these values correlated with the Braun σ^+ constants ($\rho^+ = -1.5$, which coincides with the value obtained for the thermal reaction [11] of -1.5).

Irradiation of frozen solutions of H_2PtCl_6 and phenol, hexamethylbenzene, anisole, and hydroquinone in CH_3COOH (and H_2PtCl_6 and phenol in water) with the total light from a DRSh-1000 lamp at 77°K resulted in the appearance of characteristic bands of the perpendicular orientation of Pt(III) complexes in the region of $g \approx 2.4$ in the EPR spectra (Fig. 2). The number and position of the bands in this region of the spectrum were the same for all of the systems studied. The spectra of Pt(III) complexes in the perpendicular orientation contains an intense central singlet signal from the nonmagnetic ^{196}Pt isotope and two side components caused by splitting in the ^{195}Pt isotope (natural concentration of 33.9%) [13,15]. In addition to these three bands, this region also contains a relatively weak signal with $H = 300.4$ mT which can be assigned to another complex of Pt(III). The signals of Pt(III) in the parallel orientation found in the region of $g \approx 2$ are masked by intense signals from free radicals and in some cases by the absorption induced by impurities of Mn(II). The parameters of the EPR spectra of the complexes of Pt(III) ($g_{\parallel} \approx 2$; $g_{\perp} = 2.40$; $A_{\perp} = 340 \cdot 10^{-4}$; $A_{\parallel} \sim 400 \cdot 10^{-4} \text{ cm}^{-1}$) are similar to the corresponding parameters of complexes of PtCl_6^{2-} obtained by γ -radiolysis of single crystals of K_2PtCl_6 [13]. The value of A_{\parallel} (with a precision of $\pm 50\%$) was estimated by the position of the perpendicular orientation bands using a second-order equation from perturbation theory [15]. In the region of $g \approx 2.0$, narrow singlet signals are observed in the case of phenol, hexamethylbenzene, and hydroquinone, and they can be hypothetically assigned to cation radicals or radicals of aromatic compounds. In the case of A, a triplet EPR signal is observed in this region, and it can be assigned to the PhOCH_2 radical. In irradiation of solutions of PtCl_6^{2-} and phenol or hexamethylbenzene, signals with $g \approx 4$ were observed in the EPR spectra; they could perhaps indicate the presence of dimers of paramagnetic particles or radical pairs in these systems. It should be noted that there are no EPR signals corresponding to a complex of Pt(III) and organic radicals in irradiation of a solution of PtCl_6^{2-} in CH_3COOH at 77°K. The intensity of the signals of the Pt(III) complex increases as the electron-donor capacity of the arene increases. In photolysis of frozen solutions containing PtCl_6^{2-} and PtCl_4^{2-} , signals from a Pt(III) complex also appear (but there are no signals from organic radicals).

The recording of the signals of Pt(III) complexes in the EPR spectra suggests that reaction (1) took place with the intermediate formation of such complexes. In view of the almost

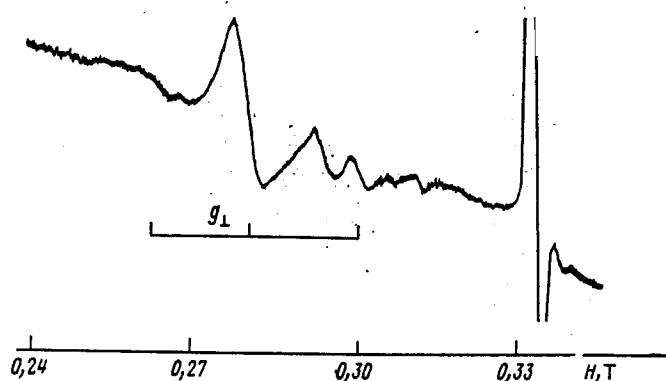
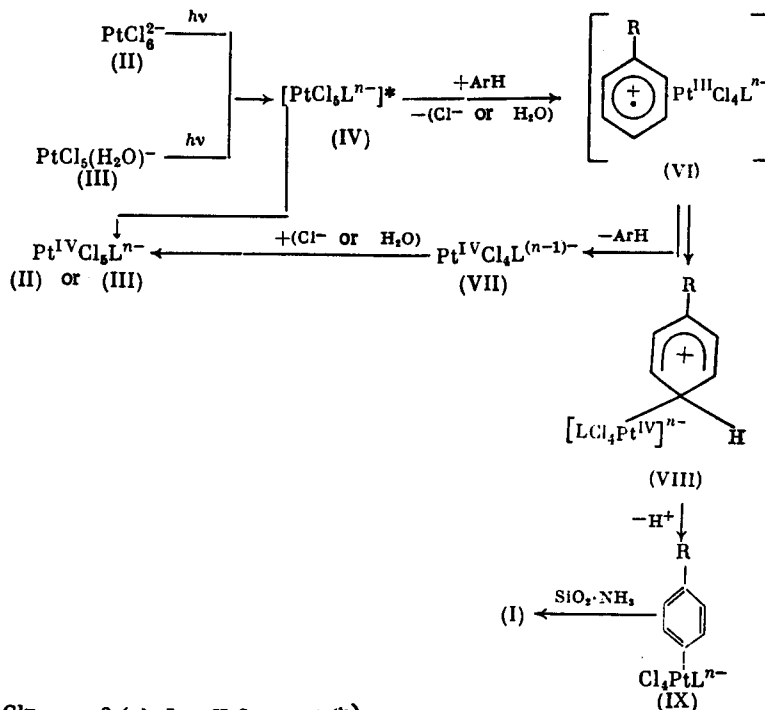


Fig. 2. EPR spectrum of a frozen solution of H_2PtCl_6 and phenol in water after irradiation at 77°K .

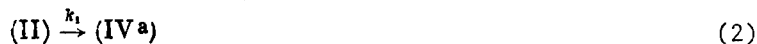
zero order of the reaction with respect to the arene and the independence of the rate of the reaction from the intensity of the light when the intensity is high enough, the following simplified scheme is proposed for describing the mechanism of the reaction.

Scheme



$\text{L} = \text{Cl}^-$, $n = 2$ (a); $\text{L} = \text{H}_2\text{O}$, $n = 1$ (b).

As shown in [16], H_2PtCl_6 is primarily present in aqueous solutions in the form of particles of (II) and (III)* in conditions similar to the conditions of our experiments, and irradiation with light sharply accelerates the mutual transition of (II) and (III). The formation of excited halogen-containing particles in single crystals of Pt(IV) complexes during irradiation with light was observed previously [17, 18]. Particles of (II) and (III) are apparently excited in the first stage of the photochemical process



Since irradiation was conducted in the spectral region which includes a charge transfer band ($\sim 365 \text{ nm}$) in chloride complexes of platinum (IV) in our experiments [14, 18], it is possible

*It is also possible that one of the coordination sites of platinum can also be occupied by carboxylic acid or its anion.

to hypothesize that particles (IVa, b) are complexes with charge transfer. In particular, one of the extreme resonance structures could be arbitrarily represented as $[\text{Pt}^{\text{III}}\text{Cl}_5(\text{Cl}\cdot)]^{2-}$ (V) (compare [14]).

Particles (IV) can subsequently either be deactivated and converted into the starting complexes



or react with the arene and form an ion radical pair (VI)

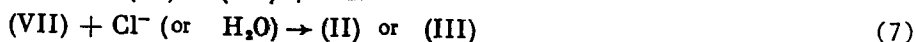


where $\text{L} = \text{Cl}^-$ or H_2O .

Generally speaking, process (5) can take place by stages with preliminary splitting of one of the ligands of complex (IV) or electron transfer and splitting of the ligand take place synchronously.

In order to avoid overloading the scheme excessively, in the subsequent discussion we will assume that the rate constants of the corresponding elementary stages of the reactions with the participation of complexes containing $\text{L} = \text{Cl}^-$ and $\text{L} = \text{H}_2\text{O}$ are the same.

Particles (VI) can either be converted into the starting complexes and free arene



or Wheland complexes can be formed and subsequently transformed into the final σ -aryl complexes (IX) and subsequently (I)



It should be noted that the presence of the stage of formation of an ion radical pair similar to (VI) is assumed in reactions of the oxidation of aromatic and alkyl aromatic hydrocarbons by the complexes of some metals [19].

The ion radical pair (VI) is converted ("collapses") into Wheland complex (VIII), whose formation is usually assumed to be an intermediate stage of electrophilic substitution. The platinum atom is only directed to the para position. The reaction of p-m-isomerization requires a high activation energy ($E_a \sim 25$ kcal/mole [12]), and there is no reversible migration of the PtCl_5 fragment to the meta position in conditions of photoinduced metallization (15-20°C). Complex (VIII) splits off a proton under the effect of a base (for example, CH_3COO^-) and is transformed into σ -aryl complex (IX). Chromatography on silica gel containing ammonia converts it into salt (I). For the reaction rate, it follows from the scheme which includes stages (2)-(9) within the framework of the method of quasi-stationary concentrations

$$W = k_6 [(\text{VI})] = \frac{k_4 k_5 [\text{ArH}] (k_1 [(\text{II})] + k_2 [(\text{III})])}{(k_5 + k_6) (k_3 + k_4 [\text{ArH}])} \quad (10)$$

Assuming $k_1 \approx k_2$ and $k_5 \gg k_6$, we obtain

$$W \approx \frac{k_1 k_4 k_5 [\text{ArH}]}{k_5 (k_3 + k_4 [\text{ArH}])} [\text{Pt}]_0 \quad (11)$$

where $[\text{Pt}]_0$ is the total concentration of the starting platinum complexes. Equation (11) qualitatively explains the weak dependence of W on $[\text{ArH}]$ and the limitation of the dependence of W on the intensity of the light with high values of I . Actually, if we assume that reactions (6) can take place both by a thermal route and possibly under the effect of light, both constants k_1 and k_5 will be proportional to I with high values of I , and W stops being dependent on I . The relatively small decrease observed in W with an increase in Cl^- could be due to the fact that the complexes with $\text{L} = \text{H}_2\text{O}$ are actually slightly more reactive than the complexes with $\text{L} = \text{Cl}^-$.

The alternative mechanism in which the $\text{Cl}\cdot$ radical is responsible for the reaction (as in the case of photooxidation of the free radical acceptor MeOH by the PtCl_5^{2-} ion [14]) is less probable. Actually, the reaction should take place according to a chain radical mechanism with a quantum yield >1 in this case and with low selectivity, which is not in agreement with the experimental data obtained.

We note that σ -aryl complexes of Pt(IV) are also formed in γ -irradiation of solutions of PtCl_6^{2-} and arenes in CH_3COOH , and signals of Pt(III) complexes are observed in the EPR spectrum of such solutions at 77°K. Since it is known that γ -radiolysis is a convenient method of generating Pt(III) compounds [20, 21], these experiments support the scheme of a reaction involving Pt(III) complexes. The formation of σ -complexes of Pt(IV) induced by γ -irradiation will be described in detail in special communications. It is also possible that the reactions of the PtCl_6^{2-} ion both with arenes and with olefins [6, 22], acetone, and alkanes [6] induced by light and γ quanta take place through the stage of formation of $[\text{RH}]^+$. $[\text{Pt(III)}]$ ion radical pairs.

CONCLUSIONS

The proposed mechanism of the photoinduced reaction of the PtCl_6^{2-} ion with an arene in acetic or aqueous trifluoroacetic acid, completed by the formation of a platinum (IV) σ -aryl complex, includes a stage of electron transfer from the arene to platinum(IV) and the formation of an ion radical pair which is then transformed into a Wheland complex.

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