THE REACTION OF PtCl$_6^{2-}$ WITH AROMATIC COMPOUNDS TO AFFORD ANIONIC σ-ARYL COMPLEXES OF PLATINUM(IV)

VIII *. KINETICS AND MECHANISMS OF THERMAL, PHOTOCHEMICAL AND γ-INDUCED REACTIONS WITH ARENES AND ARYLMERCURY COMPOUNDS (ELECTROPHILIC SUBSTITUTION INVOLVING ELECTRON TRANSFER)

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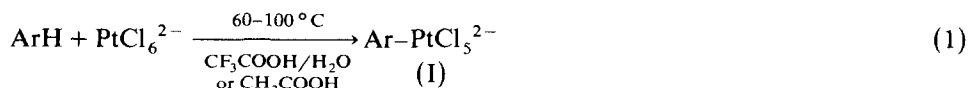
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Summary

The kinetics of the thermal reaction of the PtCl$_6^{2-}$ ion with various aromatic compounds in CF$_3$COOH/H$_2$O or CH$_3$COOH to afford σ-aryl complexes of platinum(IV) have been studied at temperatures of 60–100°C. The reaction is first order both in PtCl$_6^{2-}$ and arene. The process of formation of platinated toluene (as well as some other complexes) is accompanied with its *para-meta* isomerisation. The rate of formation of the σ-aryl complexes decreases with increasing concentration of LiCl added to the reaction mixture. Additions of AgNO$_3$, Na$_2$PtCl$_4$, Hg(OCOCH$_3$)$_2$, NaOCOCH$_3$, BF$_3 \cdot$ OEt$_2$ and SeO$_2$ accelerate the reaction. The activation energies of the formation and the *para-meta* isomerisation are ca. 100 kJ mol^{-1}. The relative rates of the reaction with different aromatic compounds (C$_6$H$_5$X) decrease in the following sequence of X: OH > OCH$_3$ > CH$_3$ > C$_2$H$_5$ > OC$_6$H$_5$ > CH(CH$_3$)$_2$ > H > C$_6$H$_5$ > F > COCH$_3$ > COOH > Cl > NO$_2$. The logarithms of the relative rates correlate with Hammett's σ and Brown's σ$^+$ constants ($\rho = -3.0$ and $\rho^+ = -1.5$). The kinetic hydrogen isotope effect of the reaction is small (~ 3 for benzene and ~ 2.3 for toluene). The following mechanism of the reaction is proposed. The first stage is the dissociation of PtCl$_6^{2-}$ followed by coordination with arene to form a π-complex. The π-complex then transforms into a Wheland-type complex, which gives a σ-aryl complex of platinum(IV) after proton elimination. The reaction of PtCl$_6^{2-}$ with arenes may be carried out at room temperature if it is induced by light or γ-irradiation. The relative rates of the photoinduced reaction decrease in the following sequence: OH > OC$_2$H$_5$ > OCH$_3$ > OC$_6$H$_5$ > CH$_3$ ($\rho^+ = -1.5$). The isotope effect for the reaction with toluene ($k_H/k_D \sim 2$) was determined. No *para-meta*

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* For parts I–VII see refs. 1–7.

isomerisation was observed in the photoinduced reaction at room temperature. The ESR spectra of frozen solutions of $PtCl_6^{2-}$ and arenes irradiated at 77 K exhibited signals due to platinum(III) complexes and organic radicals. The proposed mechanism involves electron transfer from an arene to a platinum(IV) complex to give an intermediate ion-radical pair, $[ArH]^+ [Pt^{III}Cl_5^{2-}]$. The latter may then be transformed into a Wheland-type complex. Such a mechanism may be termed the $S_E2e.t.$ mechanism. The thermal reaction of $PtCl_6^{2-}$ with Ar_2Hg in aqueous acetone to afford σ-aryl complexes of platinum(IV) is first order in the platinum(IV) complex and zero order in the aryl mercurial. The rate of the reaction decreases upon addition of LiCl. The mechanism of the reaction with Ar_2Hg appears to involve an electron-transfer stage.

Introduction

In 1979 we reported that heating a solution of $PtCl_6^{5-}$ ion and an aromatic compound in aqueous trifluoroacetic or acetic acid leads to the formation of a σ-aryl complex of platinum(IV), which can be isolated in the form of an ammonia adduct after chromatography on silica gel containing ammonia [1-7]:

$$ArH + PtCl_6^{2-} \xrightarrow[\substack{CF_3COOH/H_2O \\ or\ CH_3COOH}]{60-100\,^{\circ}C} \underset{(I)}{Ar-PtCl_5^{2-}} \tag{1}$$

$$Ar-PtCl_5^{2-} \xrightarrow{SiO_2 \cdot NH_3} \underset{(II)}{[ArPtCl_4NH_3]^-} \tag{2}$$

Complexes II are stable, solid compounds and the yields of reaction 1-2 are high (up to 80-90%) so that reaction 1-2 is a convenient way to prepare σ-aryl complexes of platinum(IV) [1-4]. Complexes II may also be obtained by the reaction of $PtCl_6^{2-}$ with aryl derivatives of Hg [7-10], Sn [7,9,10], Pb [7,9,10], B [7,10,11] and Pt^{II} [12]. The structures of complexes II with naphthalene and *ortho*-nitrotoluene were established by X-ray analysis [5]: the platinum atom is octahedrally coordinated with four chlorine atoms in the equatorial plane, and aryl and NH_3 in apical *trans*-positions. The ^{195}Pt NMR spectra of a series of complexes II have been analysed [6]. On prolonged heating, the σ-aryl complexes (both I and II) decompose to form biaryls and chlorinated aromatic compounds, platinum(IV) being reduced to platinum(II) [2,7]. The complexes react with olefins to afford arylated olefins [7,9-11,13,14].

More recently, we have found that light [15,16] or γ-irradiation [17] of a solution of $PtCl_6^{2-}$ ion and an arene in CH_3COOH or CF_3COOH/H_2O at room temperature also affords the anionic σ-aryl complexes. Some other photochemical reactions of $PtCl_6^{2-}$ with organic compounds (acetone, alkyl derivatives of tin and germanium, olefins, hexane) have been described [18-22].

In the present paper, we report the kinetics and discuss the mechanisms of the thermal, photochemical and γ-induced reactions of $PtCl_6^{2-}$ with arenes as well as with arylmercury compounds. Some parts of this work have been published as preliminary communications [15-17, 23-27].

Results and discussion

Thermal reaction with arenes

We have studied the kinetics of the thermal reaction of $PtCl_6^{2-}$ with a series of aromatic compounds in organic acids (CH_3COOH or CF_3COOH/H_2O) at various temperatures. The kinetics were followed by measuring the time dependence of the yields of complex II. Plots of the yields of complex II formed in the reactions of
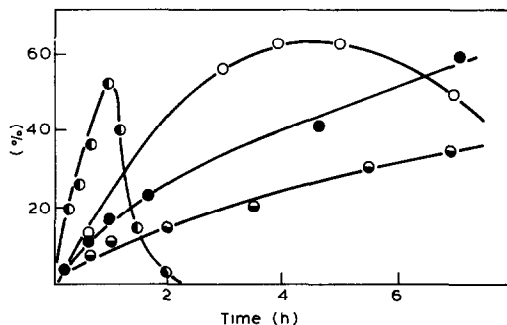

Fig. 1. Plots of the yield of complex II in the thermal reaction of H_2PtCl_6 (0.074 M) with benzene (1.75 M) in CF_3COOH/H_2O (5/1 v/v) vs. time at 70 °C (◔); 79.5 °C (●); 82 °C (○) and 85 °C (◑).
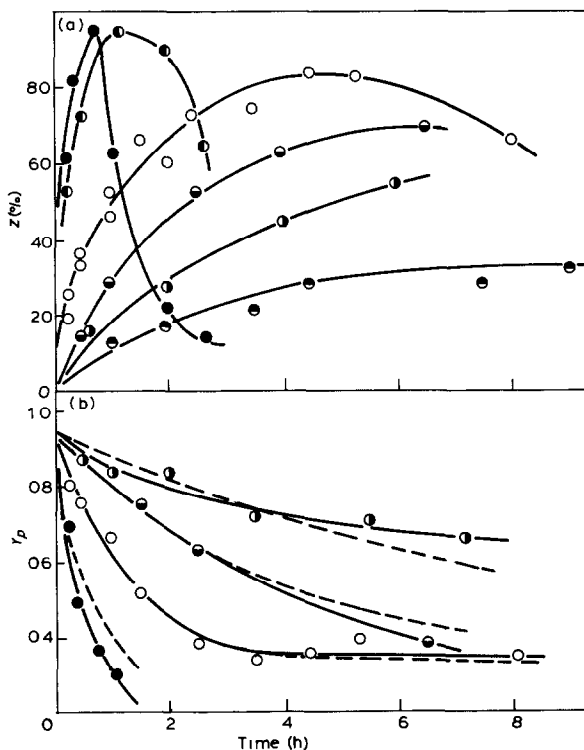

Fig. 2. Plots of the yield of complex II (a) and the relative content of p-isomer Y_p (b) in the thermal reaction of H_2PtCl_6 (0.074 M) with toluene (1.54 M) in CF_3COOH/H_2O (5/1 v/v) vs. time at 62 °C (◔); 70 °C (◕); 77 °C (◔); 85 °C (○); 93 °C (◑) and 96.5 °C (●). The dotted lines are the theoretical curves calculated using the data in Table 2 and eq. 16.

H_2PtCl_6 with benzene, toluene, anisole, biphenyl, chlorobenzene and acetophenone are shown in Figs. 1–6.

All the kinetic curves obtained are similar in character, the initial region of complex formation being followed by the region of its decay. The decomposition of complex I results in the formation of $PtCl_4^{2-}$ and products of arene oxidation. The kinetics of the formation of the σ-tolyl complex in the reaction of $PtCl_6^{2-}$ with toluene has been investigated in detail because the yield of the σ-complex in this case is very high and the relative amounts of the *para*- and *meta*-platinated isomers (no *ortho* isomers are formed for steric reasons) formed can be easily measured by means of ^1H NMR spectroscopy.

The relative content of the *para* isomer Y_p was found to decrease in the course of

$$Y_p = \frac{\left[\, p\text{-}CH_3C_6H_4\text{-}Pt^{IV}\,\right]}{\left[\, p\text{-}CH_3C_6H_4\text{-}Pt^{IV}\,\right] + \left[\, m\text{-}CH_3C_6H_4\text{-}Pt^{IV}\,\right]} \tag{3}$$
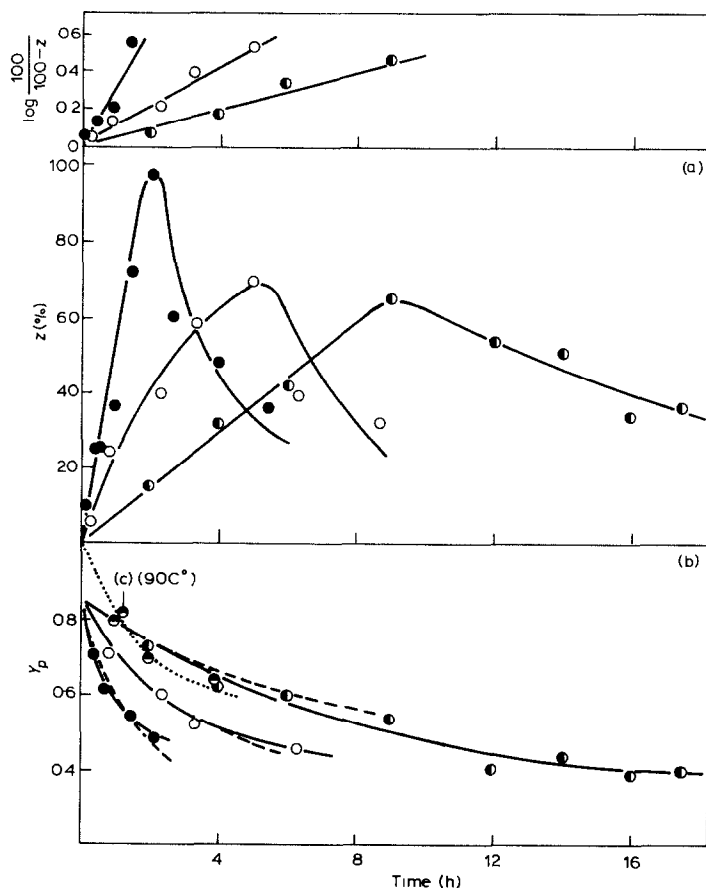

Fig. 3. Plots of the yield of complex II (a) and the relative content of *p*-isomer Y_p (b) in the thermal reaction of H_2PtCl_6 (0.08 M) with toluene (1.46 M) in CH_3COOH/H_2O (10 M) vs. time at 80 °C (◑); 90 °C (○) and 96.5 °C (●). The dotted lines are the theoretical curves calculated using the data in Table 2 and eq. 16. Isomerisation of the pure *p*-isomer is also shown (c).

the reaction, which suggests that the σ-complex formation is accompanied with its *para-meta* isomerisation (see Fig. 3b). Extrapolation of the corresponding curves to $t = 0$ allows the initial value of Y_p to be estimated: $Y_p \simeq 0.8\text{--}1.0$. With increasing time of the reaction, the value of Y_p tends to ca. 0.3, which corresponds to statistical distribution of the *para* and *meta* isomers (i.e. 1/2). Thus, kinetic control is operating at the beginning of the reaction while a thermodynamically controlled
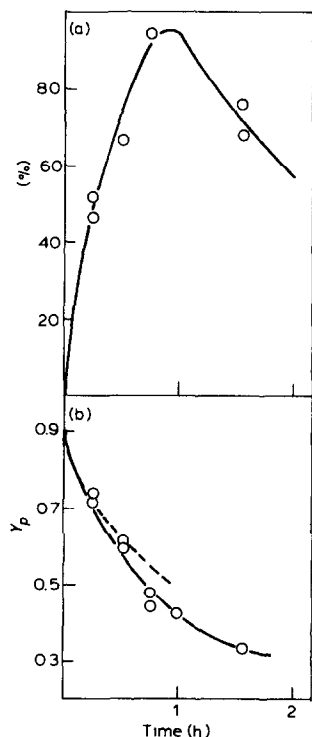

Fig. 4. Plots of the yield of complex II (a) and the relative content of *p*-isomer Y_p (b) in the thermal reaction of H_2PtCl_6 (0.13 M) in anhydrous CH_3COOH at 96.5 °C vs. time.
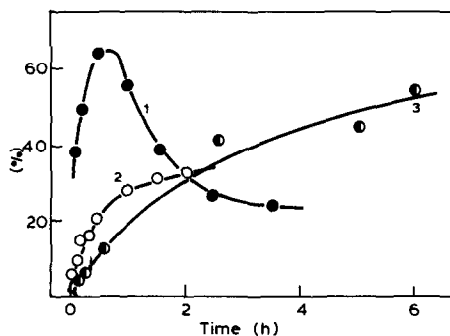

Fig. 5. Plots of the yield of complex II in the thermal reaction of H_2PtCl_6 (0.074 M) with anisole (2.0 M, 84 °C) (1), biphenyl (0.38 M, 84 °C) (2) and chlorobenzene (1.8 M, 94 °C) (3) in CF_3COOH/H_2O (6/1 v/v) vs. time.

ratio of the isomers formed is observed at large reaction times, the enthalpy of the isomerisation reaction being close to zero.

The σ-complex formation reaction is first order both in $PtCl_6^{2-}$ and arene. Indeed, the plots of the initial rates of formation of the σ-tolyl and σ-phenyl complexes versus the initial concentrations of $PtCl_6^{2-}$ and ArH are straight lines (Figs. 7 and 8). Similarly, a linear dependence is observed between the time of reaction and $\ln\{[Pt^{IV}]_0/([Pt^{IV}]_0 - [\sigma\text{-Ar-Pt}^{IV}])\} = \ln(1 - z)$, where z is the yield of complex II and $[Pt^{IV}]_0$ is the total concentration of platinum(IV) complexes ($[ArH]_0 \gg [Pt^{IV}]_0$). The effective rate constants obtained from these plots are equal, within experimental error. Hence the initial rate of the reaction W_0 can be written as

$$W_0 = k_{obsd}[Pt^{IV}]_0[ArH]_0 \tag{4}$$

The dependence of the rate of reaction 1 on the concentrations of various substances added to the reaction mixture was studied. The value of W_0 (measured as
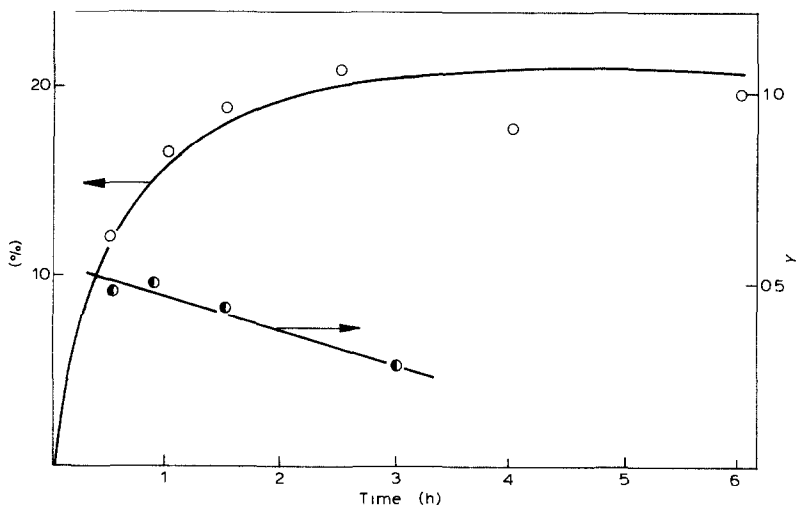

Fig. 6. Plots of the yield of complex II and the relative content of one of isomers (apparently the m-isomer) in the thermal reaction of H_2PtCl_6 (0.08 M) with acetophenone (1.3 M) in CF_3COOH/H_2O (5/1 v/v) vs. time at 96 °C.
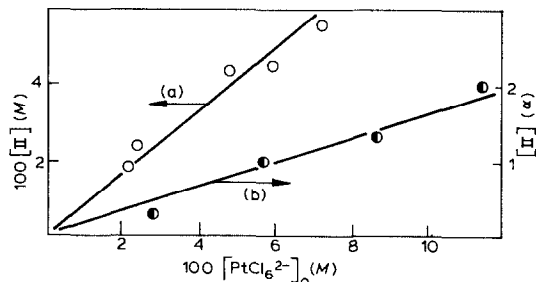

Fig. 7. Plot of the initial rate (concentration of II at 0.5 h reaction time) of the thermal reaction of H_2PtCl_6 with toluene (1.46 M) (a) and benzene (b) in CF_3COOH/H_2O (5/1 v/v) at 93 °C vs. $[PtCl_6^{2-}]_0$. α-arbitrary units.

the yield of complex II in 40 min of the reaction time) decreases with increasing concentration of LiCl added (Fig. 9). The experimental dependence of $1/W_0$ on $[Cl^-]_{add}$ is approximately linear. The addition of $AgNO_3$ results in an increase of W_0, apparently due to the withdrawal of Cl^- anions by Ag^+ (Fig. 10). The reaction rate decreases with increasing content of water in the solvent (Fig. 11). When
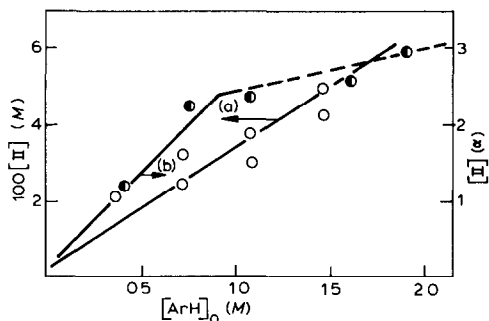

Fig. 8. Plot of the initial rate (concentration of II at 0.5 h reaction time) of the thermal reaction of H_2PtCl_6 (0.024 M) with toluene in CF_3COOH/H_2O (5/1 v/v) at 93°C vs. $[C_6H_5CH_3]_0$ (a) and $[C_6H_6]_0$ (b). α = arbitrary units.
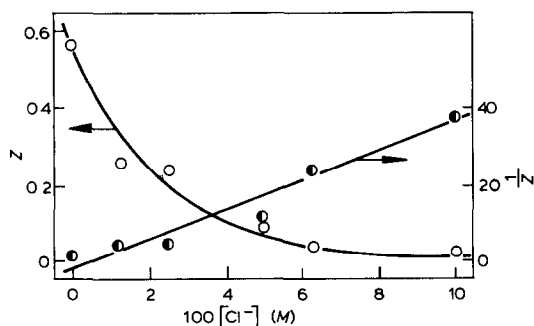
Fig. 9. Plot of the yield z (parts of 1) of complex II in the thermal reaction of H_2PtCl_6 (0.06 M) with toluene (1.34 M) in CF_3COOH/H_2O (4.5/1 v/v) (93°C, 40 min reaction time) vs. the concentration of Cl^- added.
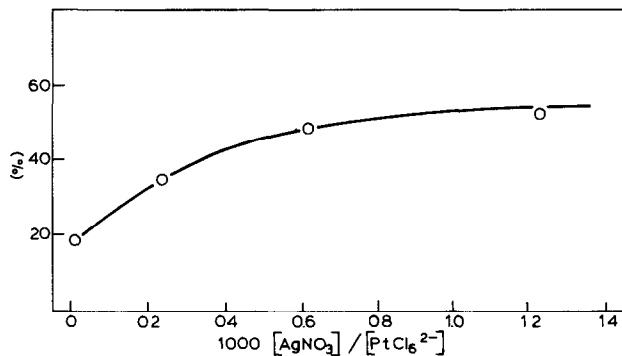

Fig. 10. Plot of the yield of complex II in the thermal reaction of H_2PtCl_6 (7.40×10⁻² M) with toluene (1.46 M) at 15 min reaction time in CF_3COOH/H_2O (6/1 v/v) vs. $[AgNO_3]/[H_2PtCl_6]$.

Na$_2$PtCl$_4$ and Hg(OCOCH$_3$)$_2$ are added to the reaction mixture the reaction is accelerated (Figs. 12 and 13). Increase of the solvent acidity by the addition of BF$_3 \cdot$ OEt$_2$ leads to an increase in the reaction rate (Fig. 14). However, if sodium acetate is added, the rate of the reaction is also increased (Fig. 15). Strong oxidants (SeO$_2$ and p-quinone) accelerate the reaction (Figs. 16 and 17). Molecular chlorine apparently promotes the cleavage of the platinum(IV)–aryl σ-bond and thus decreases the yield of complex II (Fig. 18). Hydrogen peroxide and Cu(OCOCH$_3$)$_2$ do not affect the reaction rate (Fig. 19). These experimental data will be discussed below when the proposed scheme of the reaction is considered.

The relative initial rates of reactions 1 and 2 in CF$_3$COOH/H$_2$O

$$V_0 = \frac{W_0(C_6H_5R)}{W_0(C_6H_6)} \tag{5}$$
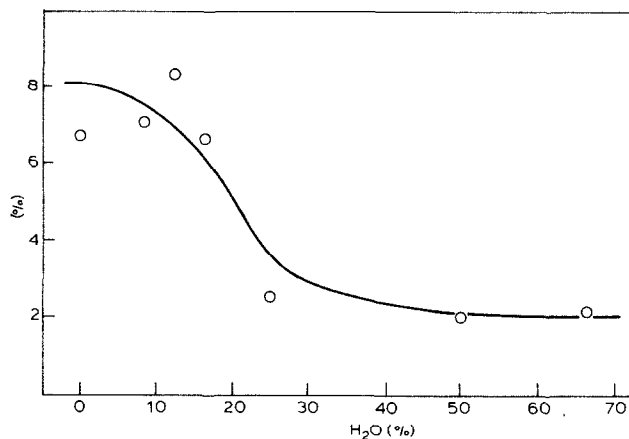
Fig. 11. Plot of the yield of complex II in the thermal reaction of H$_2$PtCl$_6$ (0.13 M) with benzene (1.85 M) in CH$_3$COOH/H$_2$O at 80 °C (2 h reaction time) vs. the water content (% v/v).

Fig. 12. Plots of the yield of complex II in the thermal reaction of H$_2$PtCl$_6$ (0.074 M) with benzene (2.2 M) in CF$_3$COOH/H$_2$O (6/1 v/v) at 84 °C (15 min reaction time) vs. the concentrations of PtCl$_4^{2-}$ (a) and Hg(OAc)$_2$ (b) (with respect to [PtCl$_6^{2-}$]).

TABLE 1

RELATIVE INITIAL RATES $V_0 = W_0(C_6H_5R)/W_0(C_6H_6)$ OF THE THERMAL REACTIONS OF $PtCl_6{}^{2-}$ WITH ARENES (C_6H_5R) IN CF_3COOH/H_2O [a]

Compound No.	R	V_0
1	OH	16
2	OCH_3	8.5
3	CH_3	3
4	C_2H_5	2.7
5	OC_6H_5	2.0
6	$CH(CH_3)_2$	1.9
7	H	1.0
8	C_6H_5	0.9
9	F	0.3
10	$COCH_3$	0.1
11	COOH	0.09
12	Cl	0.08
13	NO_2	0.04

[a] The relative rates (with respect to C_6H_6) were determined by a competitive method (90°C, 15 min). The relative rate for naphthalene is 4.3. For correlations of V_0 with σ and σ^+ see Figs. 20 and 21.
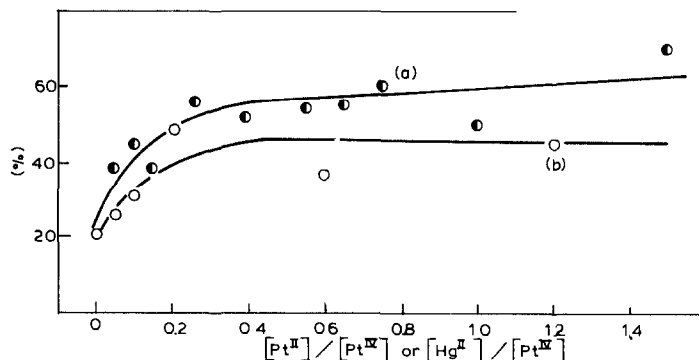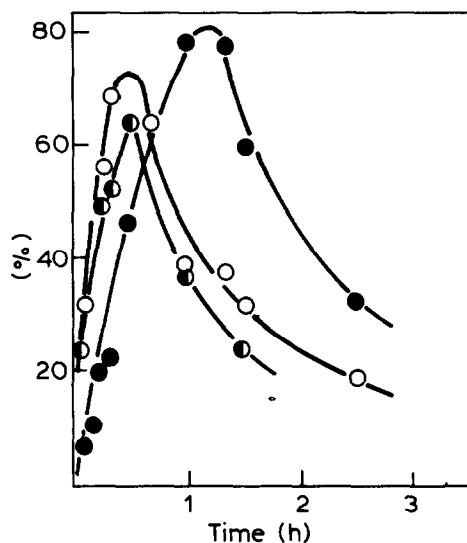

Fig. 13. Plots of the yield of complex II in the thermal reaction of H_2PtCl_6 (0.074 M) with benzene (2.2 M) in CF_3COOH/H_2O (6/1 v/v) vs. time. (●) Without additives; (○) Na_2PtCl_4 (0.025 M) added; (◐) $Hg(OAc)_2$ (0.014 M) added.

for different aromatic compounds with respect to benzene were determined using a competitive method. The results are summarized in Table 1. Partial rate factors * were determined for toluene ($f_m = 0.9$; $f_p = 16$) and acetophenone ($f_m = 0.15$; $f_p = 0.3$) on the basis of the Y_p values extrapolated to $t = 0$ (Y_p values were 0.9 and 0.5 for

* $f_m = Y_m \times 3V_0$ and $f_p = Y_p \times 6V_0$.

Fig. 14. Plot of the yield of complex II in the thermal reaction of H_2PtCl_6 (0.17 M) with benzene (1.9 M) in CH_3COOH (80 °C, 2 h reaction time) vs. $BF_3 \cdot OEt_2$ added. Total volume of reaction mixture 5 ml.
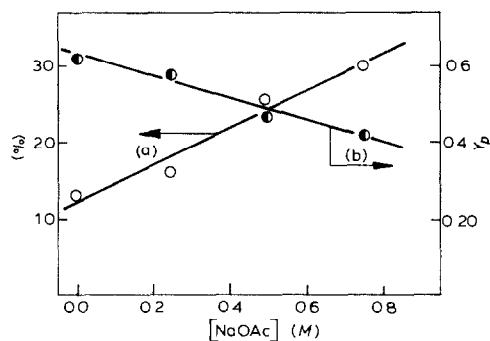
Fig. 15. Plots of the yield of complex II (a) and the relative content of p-isomer Y_p (b) in the thermal reaction of H_2PtCl_6 (8.05×10^{-2} M) with toluene (0.73 M) at 90 °C (50 min reaction time) vs. [NaOAc] added.

Fig. 16. Plot of the yield of complex II in the thermal reaction of H_2PtCl_6 (0.17 M) with benzene (1.9 M) in CH_3COOH at 80 °C (2 h reaction time) vs. the concentration of SeO_2 added.

toluene and acetophenone, respectively; see Figs. 2 and 6). The partial rate factors for the substitution at the *ortho* position, f_o, were equal to zero.

The logarithm of V_0 correlates with Hammett's σ and Brown's σ^+ constants (Figs. 20 and 21). The correlation is better if the σ or σ_p^+ values for compound Nos. 1–9 and the σ_m ($= \sigma_m^+$) constants for compound Nos. 10–13 are taken (Table 1). In this case, $\rho(\sigma) = -3.0$ and $\rho^+(\sigma^+) = -1.5$. The selectivity factor $S_f = \log(f_p^{Me}/f_m^{Me}) = 1.25$ was calculated using the data for the reaction with toluene.

The observed correlation of the logarithm of V_0 with the σ or σ^+ constants, the character of the isomers' distribution and the acceleration of the reaction with increasing acidity of the reaction medium suggest that reaction 1 may be regarded as electrophilic substitution.

Fig. 17. Plot of the yield of complex II in the thermal reaction of H_2PtCl_6 (0.17 M) with benzene (1.9 M) in CH_3COOH at 79.5 °C. (O) Without additives and (◑) with p-quinone (8.3×10^{-3} M) added at 45 min reaction time (denoted by an arrow) vs. time.
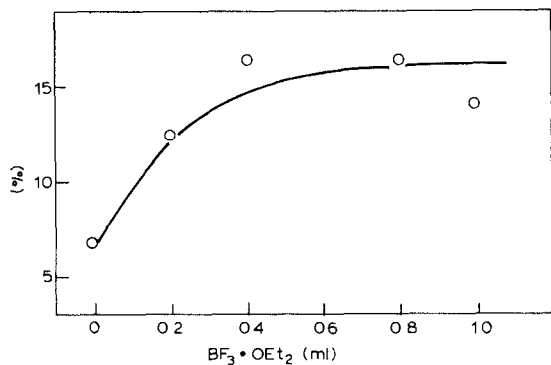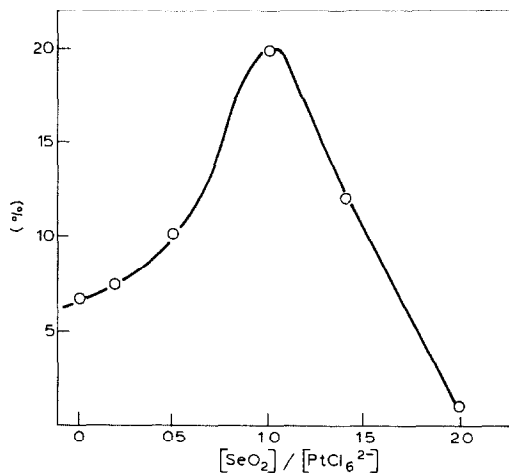

Fig. 18. Plot of the yield of complex II in the thermal reaction of H_2PtCl_6 (0.17 M) with benzene (1.9 M) in CH_3COOH at 80 °C (120 min reaction time) vs. the concentration of Cl_2 dissolved.

To account for the main experimental data obtained, i.e. the first order of the reaction in platinum(IV) and arene concentrations and the observed dependence of the reaction rate on the concentration of the Cl^- ions added, the following simplified scheme for the formation of σ-complexes can be proposed (Scheme 1).

SCHEME 1

$$PtCl_6^{2-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PtCl_5^- + Cl^- \tag{6}$$

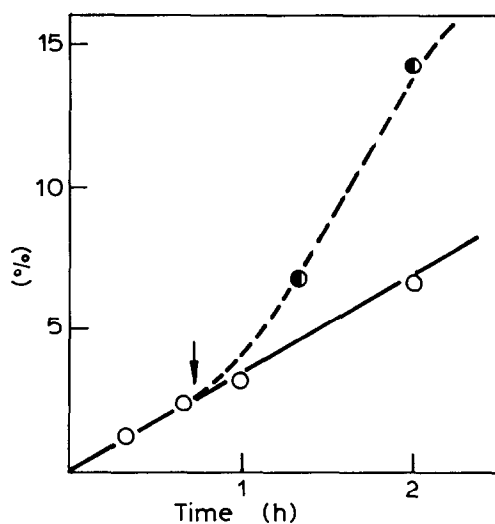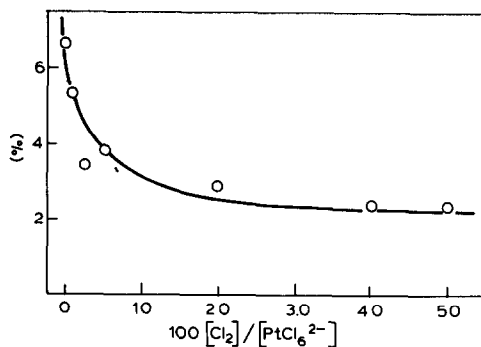$$PtCl_5(H_2O)^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} PtCl_5^- + H_2O \tag{7}$$
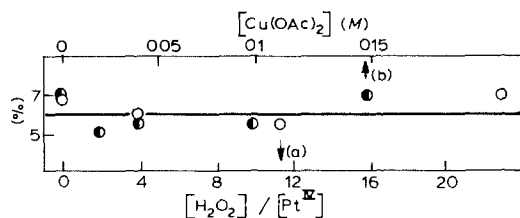

Fig. 19. Plots of the yield of complex II in the thermal reaction of H_2PtCl_6 (0.17 M) with benzene (1.9 M) in CH_3COOH at 80 °C (2 h reaction time) vs. the concentration of H_2O_2 (a) or $Cu(OAc)_2$ (b) added.
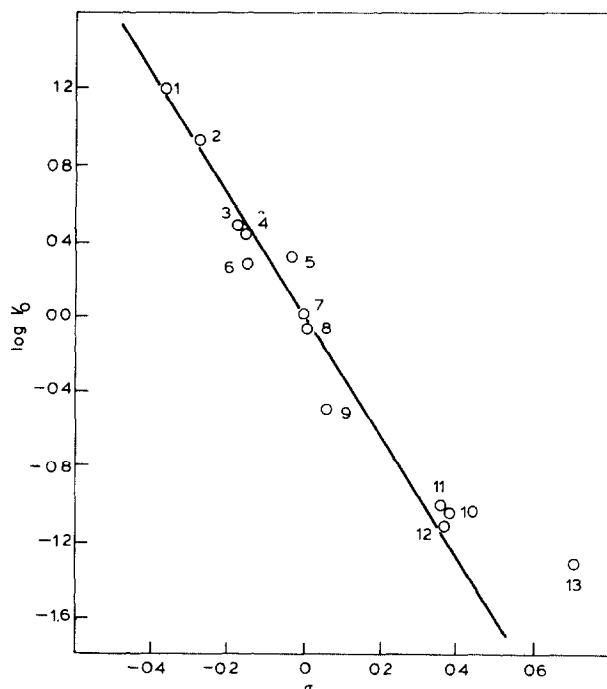

Fig. 20. Plot of the logarithm of V_0 for reaction (1)-(2) vs. σ. For compound numbers see Table 1.

$$PtCl_5^- + ArH \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \left[\pi\text{-}(ArH)PtCl_5\right]^- \tag{8}$$

$$\left[\pi\text{-}(ArH)PtCl_5\right]^- \overset{k_4}{\rightarrow} \sigma\text{-}ArPtCl_5^{2-} + H^+ \tag{9}$$
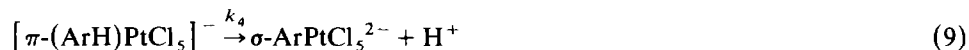
Two kinds of platinum(IV) complexes are involved in this scheme due to the fact that in acidic aqueous solutions at 60–100 °C hexachloroplatinic acid exists in the forms of $PtCl_6^{2-}$ and $PtCl_5(H_2O)^-$, the concentrations of both complexes being comparable [28,29]. In order to simplify the following calculations, we do not consider the possible reactions involving $PtCl_4(H_2O)^-$ species:

$$PtCl_5(H_2O)^- \rightleftarrows PtCl_4(H_2O) + Cl^- \text{ etc.} \tag{10}$$

Disregard of these reactions will not affect the principal conclusions of the subsequent analysis. For the same reasons, we will neglect the possible formation of platinum(IV) complexes with carboxylate anions and their reactions with arenes. It should be noted, however, that the addition of very large amounts of sodium acetate (see Fig. 15) accelerates the reaction apparently because of the involvement of such complexes in the process.

The kinetic analysis of Scheme 1 in quasi-equilibrium approximation leads to the following expression for the initial rate of complex II formation:

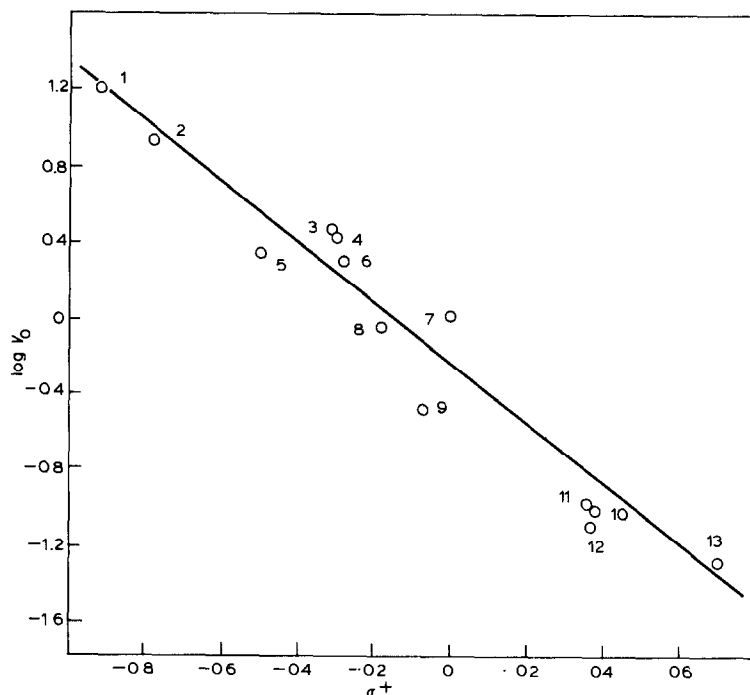$$W_0 \simeq k_{eff} \left\{ [Pt^{IV}]_0 [ArH]_0 / (K + [Cl^-]) \right\}, \tag{11}$$

Fig. 21. Plot of the logarithm of V_0 for reaction (1)-(2) vs. σ^+. For compound numbers see Table 1.

where

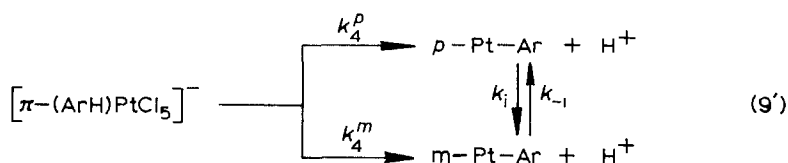$$k_{\text{eff}} = \frac{k_1 k_3 k_4}{k_{-1} k_{-3}} \tag{12}$$

and

$$K = \frac{\left[PtCl_5(H_2O)^-\right]\left[Cl^-\right]}{\left[PtCl_6{}^{2-}\right]} = \frac{k_1 k_{-2}}{k_{-1} k_2}[H_2O] \tag{13}$$

K being the equilibrium constant of the $PtCl_6{}^{2-}$ equation:

$$PtCl_6{}^{2-} + H_2O \rightleftarrows PtCl_5(H_2O)^- + Cl^- \tag{14}$$

Equation 11 is consistent with the observed first order of the reaction in $[Pt^{IV}]_0$ and $[ArH]_0$, as well as with the experimental dependence of k_{obsd} on the concentration of the chloride anions.

To account for the formation of *para* and *meta* isomers of the σ-complexes and their interconversion, reaction 9 should be presented as follows:

$$\left[\pi-(ArH)PtCl_5\right]^- \quad \xrightarrow{\qquad} \quad \begin{array}{c} \xrightarrow{k_4^p} \quad p-Pt-Ar \; + \; H^+ \\ \quad k_i \updownarrow k_{-i} \\ \xrightarrow{k_4^m} \quad m-Pt-Ar \; + \; H^+ \end{array} \tag{9'}$$

so that the overall scheme of the process can be written as follows (Scheme 2). In this

$$ArH \; + \; Pt^{IV} \quad \xrightarrow{\qquad} \quad \begin{array}{c} \xrightarrow{k_{\text{obsd}}^p} \quad p-Pt-Ar \\ \quad k_i \updownarrow k_{-i} \\ \xrightarrow{k_{\text{obsd}}^m} \quad m-Pt-Ar \end{array}$$
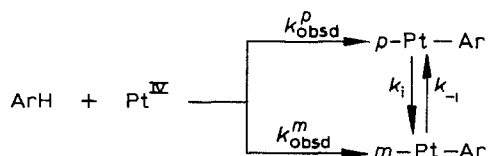
SCHEME 2

scheme, Pt^{IV} denotes the starting chloride or aquachloride complex of platinum(IV).

For the reaction with toluene, the observed enthalpy of isomerisation is close to zero, $\Delta H \simeq 0$ (see above), which suggests that

$$k_i \simeq 2k_{-i} \tag{15}$$

If eq. 15 is taken into account, the kinetic analysis of Scheme 2 (see Appendix) gives the following expression for the time dependence of the *para* isomer content (see eq. 3):

$$Y_p = \tfrac{1}{3} + \frac{6\kappa_p - 2\kappa}{3(2\kappa - 3k_i)} \times \frac{e^{-(3/2)k_i t} - e^{-\kappa t}}{1 - e^{-\kappa t}} \tag{16}$$

where t is the time and κ is the pseudo-unimolecular rate constant of the σ-complex formation:

$$\kappa = k_{\text{obs}}[C_6H_5CH_3]_0 \tag{17}$$

TABLE 2

KINETIC PARAMETERS OF THE FORMATION AND THE *para-meta* ISOMERISATION OF THE σ-TOLYL COMPLEX OF PLATINUM(IV) [a]

Solvent	T ($^\circ$C)	$10^5 k_{obsd}$ ($M^{-1}\,s^{-1}$)	E_a of formation (kJ mol^{-1})	$10^5 k_i$ (s^{-1})	E_a of isomerisation (kJ mol^{-1})
CF$_3$COOH/H$_2$O	62	1.62			
(9.2 M)	70	3.24		4.17	
	77	5.38	100 ± 20	10.0	110 ± 20
	85	18.2		26.0	
	93	35.0			
	96.5	46.7		69.0	
CH$_3$COOH/H$_2$O	80	1.51		3.9	
	90	4.38	125 ± 20	9.7	90 ± 20
	96.5	9.73		14.2	
CH$_3$COOH	96.5	41.0		41.7	

[a] See Figs. 2, 3, 4 and 22; Scheme 2 and eqs. 15 and 17–19. Accuracy: $\pm 30\%$ for k_{obsd} and $\pm 20\%$ for k_i.

$$\kappa = \kappa_m + \kappa_p \tag{18}$$

$$k_{obsd} = k^p_{obsd} + k^m_{obsd} \tag{19}$$

The kinetics of the reaction of PtCl$_6^{2-}$ with toluene was studied in aqueous CF$_3$COOH, aqueous CH$_3$COOH and anhydrous CH$_3$COOH. The κ values were determined from the initial slopes of the kinetic curves for the complex formation. The values of κ_p can then be calculated by extrapolating the plots of Y_p to $t = 0$ (see Figs. 2–4): $\kappa_p = 0.95\kappa$ for the reaction in CF$_3$COOH/H$_2$O, $\kappa_p = 0.85\kappa$ for CH$_3$COOH/H$_2$O, and $\kappa_p = 0.9\kappa$ for CH$_3$COOH. Table 2 lists the experimental values of k_{obsd} in these solvents at various temperatures, as well as the best fit for the k_i parameters calculated using eq. 16.

In order to check the validity of Scheme 2, the kinetics of the isomerisation of the
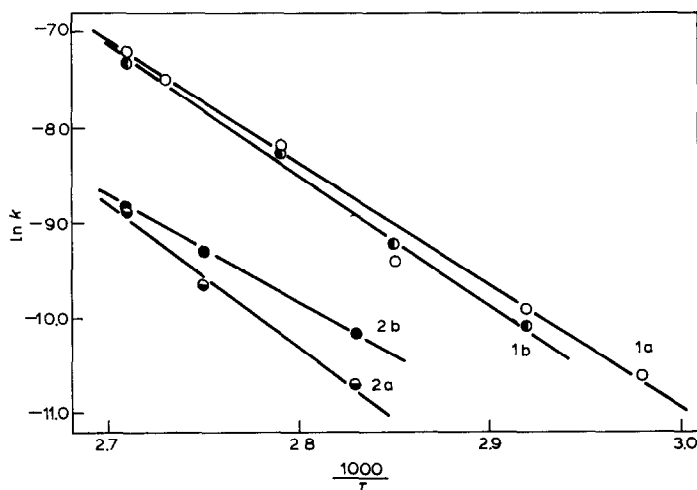

Fig. 22. Plots of ln k for the reactions of formation (a) and *para-meta* isomerisation (b) of the σ-tolyl complex of Pt^{IV} in CF$_3$COOH/H$_2$O (1) (see Fig. 2) and CH$_3$COOH/H$_2$O (2) (see Fig. 3) vs. 1/T.

pure *para* isomer prepared by the photoinduced reaction of H_2PtCl_6 with toluene in CH_3COOH/H_2O (see below) was also studied (see Fig. 3). The rate constant of this first-order reaction at $90\,^{\circ}C$ $(7.3 \times 10^{-5}\ s^{-1})$ is very close to the corresponding value of k_1 given in Table 2 $(9.7 \times 10^{-5}\ s^{-1})$. It should also be noted that the values of k_{obsd} for the reaction with toluene calculated using various experimental plots, viz. the dependence of W_0 on $[Pt^{IV}]_0$, $[C_6H_5CH_3]_0$, $[Cl^-]$ and time $(3.0 \times 10^{-4}; 3.1 \times 10^{-4}; 1.8 \times 10^{-4},$ and $3.5 \times 10^{-4}\ M^{-1}\ s^{-1}$, respectively; temperature $93\,^{\circ}C$) are in good agreement with each other. The value of equilibrium constant, $K = 4.4 \times 10^{-3}$ M (see eq. 14), calculated from the plot shown in Fig. 9 is consistent with its values at $93\,^{\circ}C$ estimated from the data of refs. 28 and 29.

The activation energies of the formation and the isomerisation of the σ-tolyl complex in CF_3COOH/H_2O and CH_3COOH/H_2O (see Fig. 22) are listed in Table 2 and are about 100 kJ mol^{-1}. The acidity of the solvent affects the reaction rates of both the formation and the *para-meta* isomerisation reactions of the σ-tolyl complex (Table 2), the increase being approximately 5 times on going from CH_3COOH/H_2O to CF_3COOH/H_2O. The addition of a strong acid such as $BF_3 \cdot OEt_2$ (see above, Fig. 14) accelerates the reaction. The increase of the reaction rate with decreasing water content (Fig. 11) may also be due to the rise of acidity. The influence of acidity on the rate of the formation of the σ-aryl complex is probably due to the shift of equilibria (6)–(8). Similar effects were observed for the reaction of electrophilic mercuration (see discussion below).

The influence of acidity on the rate of isomerisation is consistent with eq. 9′. The detailed mechanism of this reaction apparently involves the formation of an intermediate Wheland-type complex, III (see Scheme 3).

(Pt = PtCl$_5^-$ or PtCl$_4$(H$_2$O))
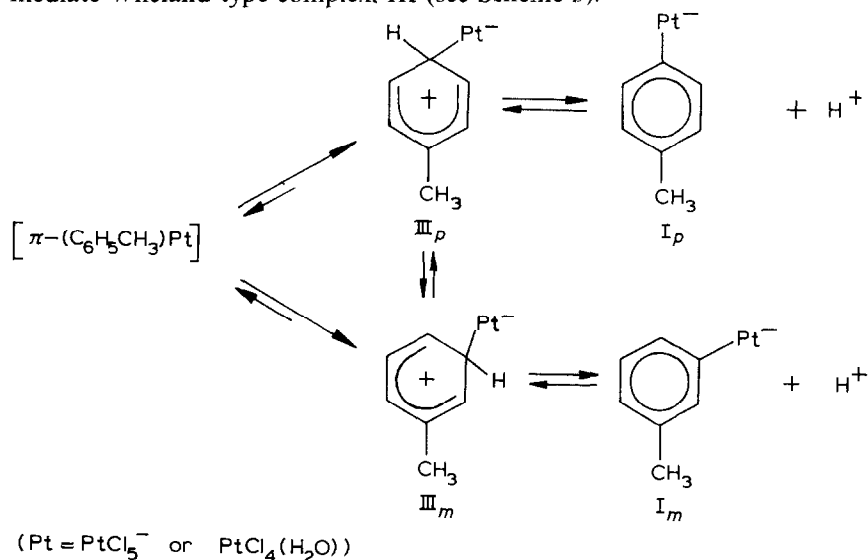
SCHEME 3

Wheland complexes are generally accepted to be intermediate active species in the reactions of electrophilic substitution in aromatic compounds [30–39]. Recently, the fluxionality of arylrhenium complexes was explained by the formation of a complex analogous to III [40,41]. The structure of a complex of this type containing platinum(II) was established by X-ray analysis [42].
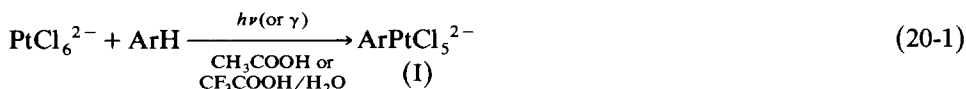
(IV)
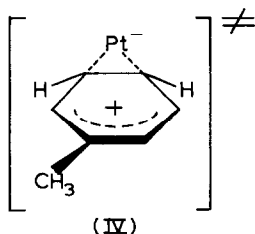
The isomerisation of the Wheland complexes $III_p \rightleftarrows III_m$ possibly proceeds through the transition state IV, and/or is due to the reversibility, to some extent, of the stage of formation of III. The transarylation reaction reported in ref. 7 is perhaps also due to the reversibility of the Wheland complex formation.

The σ-complex formation reaction reveals a primary kinetic hydrogen isotope effect, the value of k_H/k_D in CF_3COOH/H_2O being ca. 3 for benzene-d_6 at 82°C and ca. 2.3 for toluene-d_8 at 70°C. The small values of k_H/k_D suggest that the rate-limiting step of the reaction is the formation of the Wheland complex III rather than the subsequent elimination of the proton.

To end this section, the effect of adding mercury acetate and $PtCl_4^{2-}$ to the reaction mixture (see above, Figs. 12 and 13) should be discussed. The observed increase of the rate of formation of the σ-aryl complex of platinum(IV) in these cases may be due to the occurrence of another path of this reaction, viz. via the formation of the σ-aryl complexes of mercury(II) and platinum(II) followed by a transarylation reaction to afford complex I. The electrophilic metallation of arenes by mercury(II) (see below) and platinum(II) [12] is known. The accelerating effect of $Hg(OCOCH_3)_2$ may also be due to the ability of this compound to form complexes with chloride anions. In the case of platinum(II) present in the reaction system there can be one more path for the formation of the σ-aryl complex of platinum(IV), i.e. oxidative addition of the arene molecule to $PtCl_4^{2-}$. The oxidative-addition reactions of $PtCl_4^{2-}$ with alkyl iodides [43–45], aryl iodides [46] and tetramethyltin [19,47] have recently been found to form σ-organyl complexes of platinum(IV). So it might be further assumed that reaction (1) proceeds via oxidative addition of arene to $PtCl_4^{2-}$ present in the reaction mixture as an admixture [48]. This type of mechanism was also proposed for the thermal reaction of $PtCl_6^{2-}$ with alkanes [49–52]. However, this mechanism is unlikely in the case of arenes since it would predict the inhibiting effect of strong oxidants, which contradicts the experimental data on reaction (1) carried out in the presence of SeO_2 or p-quinone (see Figs. 16 and 17).

Photochemical and γ-induced reactions with arenes

Light irradiation of a solution of $PtCl_6^{2-}$ and an arene (ArH) in CH_3COOH or CF_3COOH/H_2O at room temperature affords a σ-aryl complex of platinum(IV) which can be isolated in the form II. The solutions were irradiated by the full light of a high-pressure mercury lamp (1000 W). The reaction induced by γ-irradiation (^{60}Co source) proceeds analogously [17].

$$PtCl_6^{2-} + ArH \xrightarrow[\substack{CH_3COOH \text{ or} \\ CF_3COOH/H_2O}]{h\nu(\text{or }\gamma)} ArPtCl_5^{2-} \qquad (20\text{-}1)$$
(I)

$$\text{ArPtCl}_5{}^{2-} \xrightarrow{\quad \text{SiO}_2 \cdot \text{NH}_3 \quad} [\text{ArPtCl}_4\text{NH}_3]^- \tag{20-2}$$
$$\text{(II)}$$

The kinetics of the photoinduced process were studied for anisole, toluene and naphthalene, using filters (Fig. 23). It should be noted that an induction period was observed in the case of napthalene complex I, the accumulation of this complex in the reaction mixture being accompanied with the formation of a green platinum(IV)-containing complex absorbing at ν 14400 cm^{-1}. The structure of this complex is not clear. One may suspect it to be a Wheland-type complex, III, but as yet, no experimental evidence to confirm this suggestion has been obtained. The kinetics of the σ-aryl complex formation in the γ-induced reaction was studied for anisole (Fig. 24) [17].
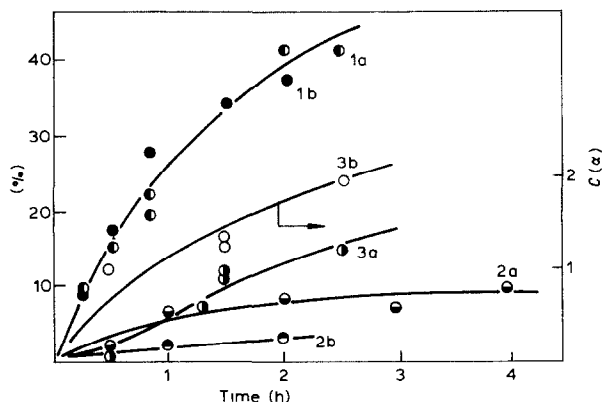
Fig. 23. Plots of the yield of complex II in the photoinduced reaction of H_2PtCl_6 (0.08 M for compounds 1,2; 0.04 M for 3) with arenes (0.64 M) vs. time. (1) Anisole in CH_3COOH/H_2O (90/1) (a) and in CF_3COOH/H_2O (4/1) (b); (2a) toluene (0.94 M) in CH_3COOH/H_2O (90/1) (2b-toluene-d_8); (3a) naphthalene (0.1 M) in CH_3COOH/H_2O (30/1); (3b) concentration (α-arbitrary units) of the complex absorbing at ν 14400 cm^{-1}. Light, 320–485 nm; 22°C.

Fig. 24. Plot of the yield of complex II in the reaction of H_2PtCl_6 (0.29 M) with anisole (0.87 M) in CH_3COOH at ~ 50°C vs. the dose of γ-irradiation.

The photoinduced reaction with anisole was investigated in detail. The yield of anisole complex II decreases with increasing initial concentration of $PtCl_6^{2-}$ (Fig. 25). The dependence of the rate of the reaction on the anisole concentration could only be reliably studied at high concentrations of anisole (Fig. 26). At low light intensity I, the rate of the reaction depends linearly on I; with increasing light intensity, the reaction rate becomes independent of I (Fig. 27). The addition of LiCl to the solution reduces the reaction rate (Fig. 28). The yield of complex II decreases with increasing content of water in the solvent (Fig. 29), though the effect of acidity of the medium on the reaction rate is less pronounced than in the case of the thermal reaction (see Fig. 23). The addition of an oxidant (SeO_2) or Na_2PtCl_4 reduces the rate of the reaction (Figs. 30 and 31).

The observed activation energy for the photoinduced reaction (20) is 21 ± 4 kJ mol^{-1} (Fig. 32). The relative rates, V_0', of reaction (20) with different aromatic
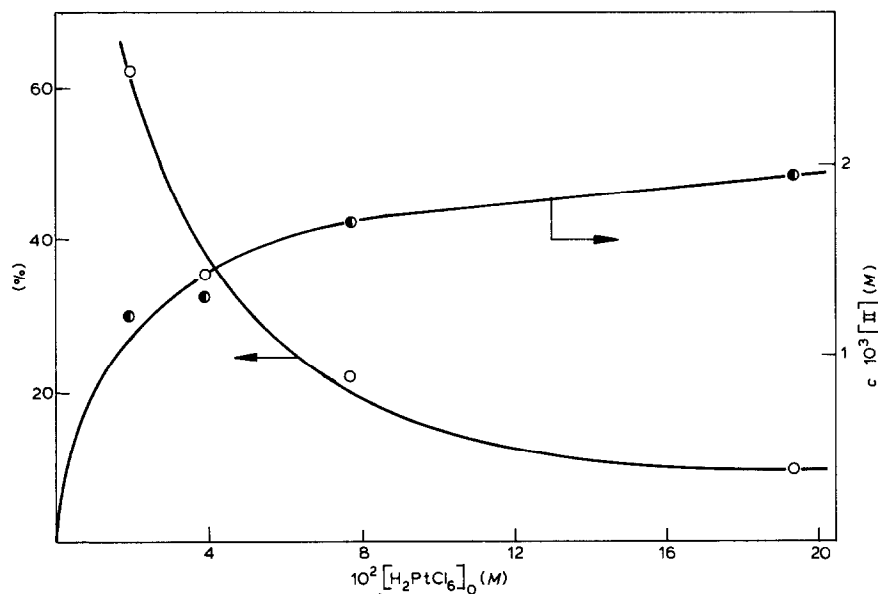
Fig. 25. Plots of the yield and concentration c (M) of complex II in the photoinduced reaction of H_2PtCl_6 with anisole (0.64 M) in CH_3COOH (50 min reaction time) vs. the initial concentration of $PtCl_6^{2-}$.
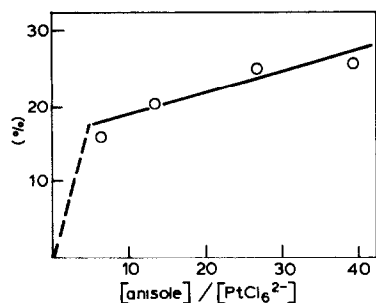
Fig. 26. Plot of the yield of complex II in the photoinduced reaction of H_2PtCl_6 (0.077 M) with anisole in CH_3COOH (50 min reaction time) vs. the relative concentration of anisole (with respect to Pt^{IV}).

compounds were determined using a competitive method. The results obtained are listed in Table 3. The logarithm of V_0' correlates with Hammett's σ and Brown's σ^+ constants ($\rho^+ = -1.5$) (Fig. 33). The relative rates for phenol and anisole in the
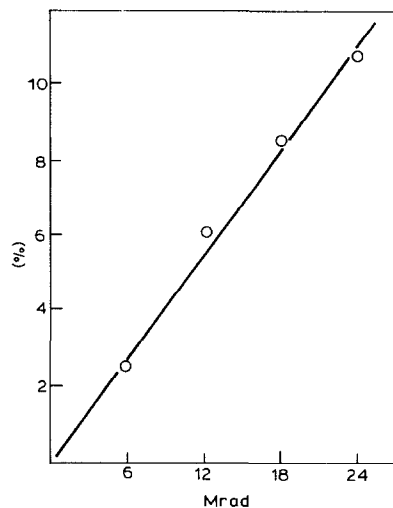

Fig. 27. Plot of the yield of complex II in the photoinduced reaction of H_2PtCl_6 (0.077 M) with anisole (0.64 M) in CH_3COOH (1 h reaction time) vs. light intensity (I 100% = full light of a high-pressure Hg lamp).
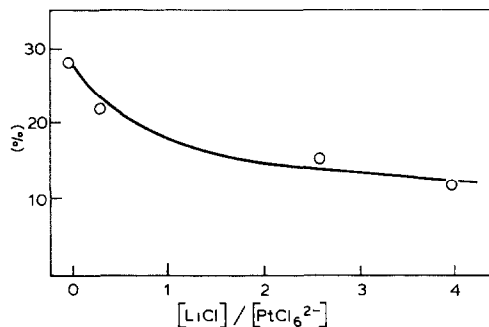
Fig. 28. Plot of the yield of complex II in the photoinduced reaction of H_2PtCl_6 (0.077 M) with anisole (0.64 M) in CF_3COOH/H_2O (4/1 v/v) (50 min reaction time) vs. the relative concentration of LiCl added (with respect to Pt^{IV}).
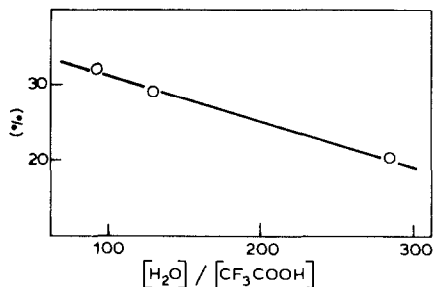
Fig. 29. Plot of the yield of complex II in the photoinduced reaction of H_2PtCl_6 (0.077 M) with anisole (0.64 M) in CF_3COOH/H_2O (50 min reaction time) vs. the water content in the solvent mixture (H_2O/CF_3COOH M/M).
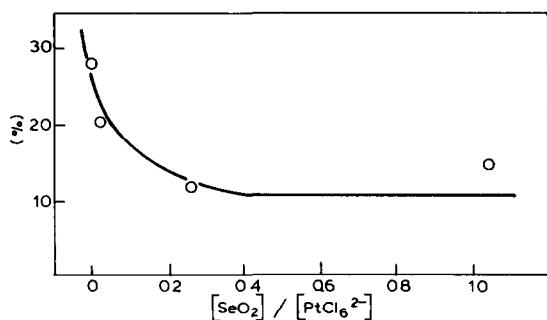
Fig. 30. Plot of the yield of complex II in the photoinduced reaction of H_2PtCl_6 (0.072 M) with anisole (0.64 M) in CF_3COOH/H_2O (4/1 v/v) (50 min reaction time) vs. the relative concentration of SeO_2 added (with respect to Pt^{IV}).
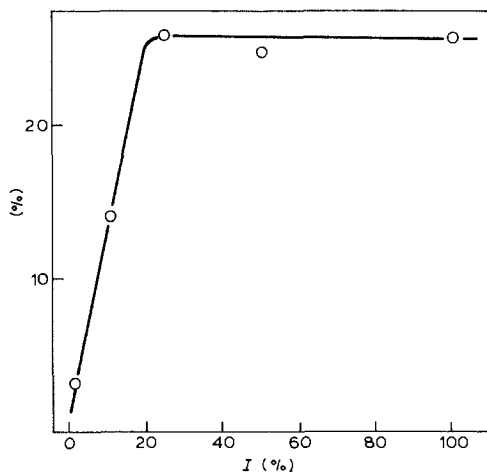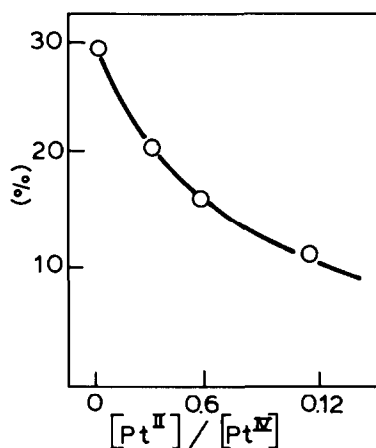

Fig. 31. Plot of the yield of complex II in the photoinduced reaction of H_2PtCl_6 (0.077 M) with anisole (0.64 M) in CH_3COOH/H_2O (21/1 v/v) (50 min reaction time) vs. the relative concentration of Na_2PtCl_4 added (with respect to Pt^{IV}).

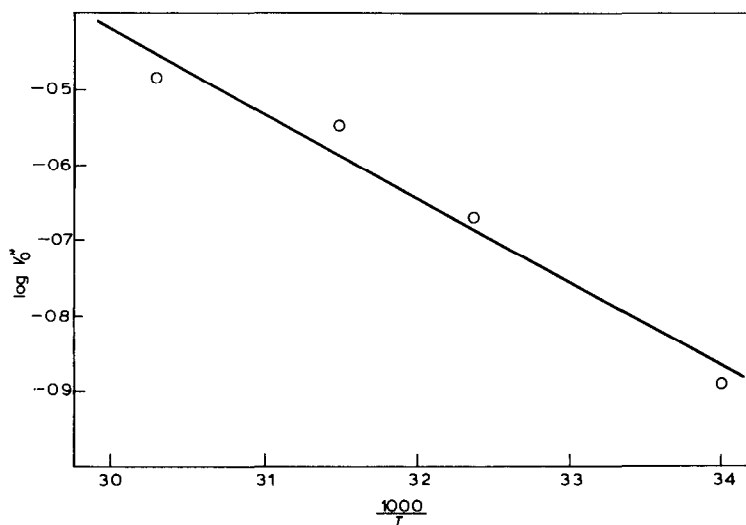Fig. 32. Dependence of log V_0'' on $1/T$ for photoinduced reaction (20) of H_2PtCl_6 (0.077 M) with anisole (0.64 M) in CH_3COOH. V_0'' are relative initial rates.

TABLE 3

RELATIVE INITIAL RATES $V_0' = W_0'(C_6H_5R)/W_0'(C_6H_6)$ OF THE PHOTOCHEMICAL REACTIONS OF $PtCl_6{}^{2-}$ WITH ARENES (C_6H_5R) IN CH_3COOH

Compound No.	R	V_0'
1	OH	8
2	OC_2H_5	4.1
3	OCH_3	4.0
4	OC_6H_5	1.9
5	CH_3	1.0

γ-induced reaction are 2.1/1 ($\rho^+ \simeq -2.3$), which is close to the data obtained for the corresponding photochemical reaction (see Table 3). The kinetic isotope effect evaluated from the kinetics of the photoinduced reaction with toluene-d_8 is $k_H/k_D \simeq 2$ (see Fig. 23). The estimated quantum yield of the photochemical reaction is 10^{-4}–10^{-6}. In contrast to the thermal reaction, the photoinduced process results in the formation of *para* isomers ($\geqslant 95\%$ according to the ^1H NMR test) of toluene and anisole complexes and no *para-meta* isomerisation is observed.

When a frozen solution of H_2PtCl_6 and arene (phenol, anisole, hexamethylbenzene, or *p*-hydroquinone) in CH_3COOH as well as H_2PtCl_6 and phenol in water is irradiated with the full light of a high-pressure mercury lamp at 77 K, ESR spectra are observed. All the spectra contain the characteristic signals of platinum(III) complexes in perpendicular orientation, in the region $g \simeq 2.4$. The number and position of the ESR signals in this region of the spectrum are the same for all the systems studied. The ESR spectra of platinum(III) complexes in perpendicular orientation consist of an intensive central signal due to the non-magnetic ^{196}Pt isotope and two satellites due to the splitting on the ^{195}Pt isotope (natural abundance 33.8%) [53–55]. In addition to these three signals, a relatively weak peak is observed in this region at H 300.4 mT; this is attributed to a platinum(III) complex of a different structure. The signals due to the platinum(III) complex in parallel
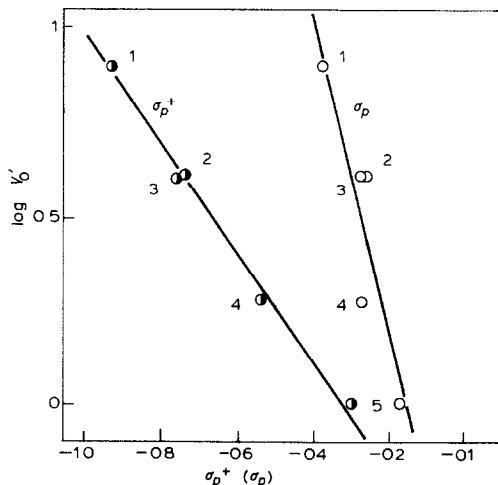

Fig. 33. Correlation of the logarithm of V_0' for photoinduced reaction (20) with σ_p^+ and σ_p. For compound numbers see Table 3.

orientation, located in the region $g \simeq 2.0$, are concealed under intensive resonances due to organic free radicals. The parameters of the ESR spectra of the platinum(III) complex in the systems under consideration ($g_{\parallel} \simeq 2.0$; $g_{\perp} = 2.40$; $A_{\perp} = 340 \times 10^{-4}$ cm^{-1}; $A_{\parallel} \sim 400 \times 10^{-4}$ cm^{-1}) are similar to those of the PtCl$_5^{2-}$ complexes obtained by γ-radiolysis of K$_2$PtCl$_4$ monocrystals [53]. The values of $A_{\parallel}$ (accuracy $\pm$ 50%) were estimated from the non-equidistant positions of the signals of the perpendicular orientation, using formulae of the second-order perturbation theory [56]. Narrow singlet signals at $g \simeq 2.0$ are observed in the spectra in the case of phenol, hexamethylbenzene and p-hydroquinone. These signals can be assigned to cation-radicals or radicals derived from aromatics. A poorly resolved triplet signal in this region, observed in the case of anisole, is probably due to the C$_6$H$_5$OCH$_2^{\cdot}$ radical. The ESR spectra of irradiated frozen solutions of H$_2$PtCl$_6$ and phenol, or H$_2$PtCl$_6$ and hexamethylbenzene contain signals at $g \simeq 4$ which may indicate the existence of dimers of paramagnetic species or radical pairs in these systems.

It should be noted that the intensity of the signals due to platinum(III) complexes increases with increasing electron-releasing ability of the arene. In the absence of arene, no signals were registered in the region $g \simeq 2.4$. Photolysis of a frozen solution containing PtCl$_6^{2-}$ and PtCl$_4^{2-}$ in CH$_3$COOH at 77 K results in the emergence of ESR signals due to platinum(III), the signals of organic radicals at $g \simeq 2$ being absent.

Analogously, γ-radiolysis (^{60}Co source, with a nominal dose rate of 6 Mrad h^{-1}) of a frozen solution of PtCl$_6^{2-}$ and anisole in CH$_3$COOH at 77 K gives rise to a composite ESR spectrum containing signals due to both a platinum(III) complex at $g \simeq 2.4$ and radicals derived from anisole at $g \simeq 2.0$, as well as several unidentified lines [17]. It should be noted that the formation of platinum(III) complexes in different reactions has been described recently in refs. 57 and 58.
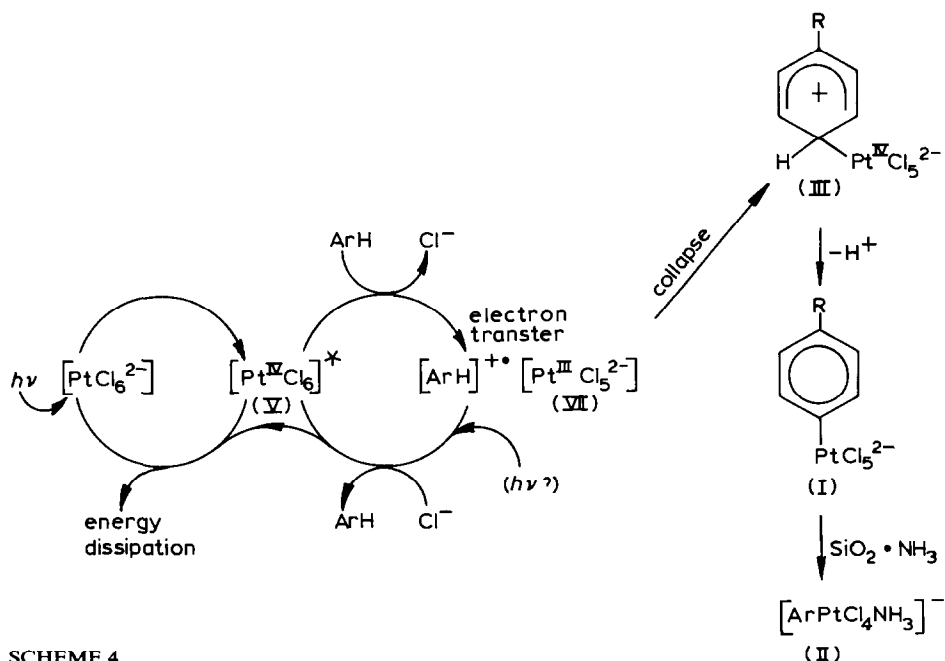
SCHEME 4

The detection of platinum(III) complexes in irradiated frozen solutions containing $PtCl_6^{2-}$ and an arene allows us to make an assumption, namely that reaction 20 proceeds via the formation of a transient platinum(III) complex. To account for the experimental data obtained, Scheme 4 is proposed for the photoinduced reaction.

Just like in the case of the thermal reaction, at least two kinds of starting platinum(IV) complexes must be considered, viz. $PtCl_6^{2-}$ and $PtCl_5(H_2O)^-$. Light irradiation is known to accelerate the interconversion between them [59].

$$PtCl_6^{2-} + H_2O \overset{h\nu}{\rightleftarrows} PtCl_5(H_2O)^- + Cl^- \tag{21}$$

We assume that the first step of reaction 20 is photoexcitation of $PtCl_6^{2-}$ or the $PtCl_5(H_2O)^-$ species (in Scheme 4, only $PtCl_6^{2-}$ is shown for simplicity).

$$PtCl_6^{2-} \overset{h\nu}{\underset{k_1}{\rightarrow}} \left[PtCl_6^{2-}\right]^\star \tag{22}$$
$$(V)$$

$$PtCl_5(H_2O)^- \overset{h\nu}{\underset{k_2}{\rightarrow}} \left[PtCl_5(H_2O)^-\right]^\star \tag{23}$$
$$(VI)$$

Excited complexes were detected earlier in light-irradiated monocrystals of platinum(IV) halogenides [60,61], their lifetimes (in the solid state) being of the order of $3 \times 10^{-4} - 8 \times 10^{-4}$ s. Since the charge-transfer band for chloride complexes of platinum(IV) lies in the region of the main emission band of the high-pressure mercury lamp (ca. 365 nm) [55,61], one can assume that species V and VI are charge-transfer complexes. This implies that one of their resonance structures is a platinum(III) complex *, e.g. $[Pt^{III}Cl_5(Cl)]^{2-}$ in the case of $[PtCl_6^{2-}]^\star$.

The excited particles V and VI are either deactivated (to simplify the scheme and subsequent calculations, we will assume the rate constants of related reactions to be the same for Cl^- and H_2O-containing intermediate particles):

$$\left[PtCl_6^{2-}\right]^\star \overset{k_3}{\rightarrow} PtCl_6^{2-} \tag{24}$$

$$\left[PtCl_5(H_2O)^-\right]^\star \overset{k_3}{\rightarrow} PtCl_5(H_2O)^- \tag{25}$$

or interact with an arene molecule to form the ion-radical pair VII or VIII:

$$\left[PtCl_6^{2-}\right]^\star + ArH \overset{k_4}{\rightarrow} [ArH]^+ \left[Pt^{III}Cl_5^{2-}\right] + Cl^- \tag{26}$$
$$(VII)$$

$$\left[PtCl_5(H_2O)\right]^\star + ArH \overset{k_4}{\rightarrow} [ArH^{+\cdot}]\left[Pt^{III}Cl_4(H_2O)^-\right] + Cl^- \tag{27}$$
$$(VIII)$$

$$\left[PtCl_5(H_2O)\right]^\star + ArH \overset{k_4}{\rightarrow} VII + H_2O \tag{28}$$
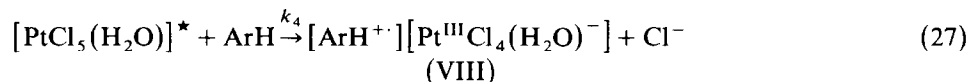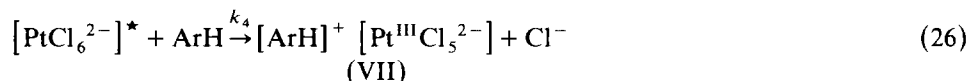
A possible mechanism of reaction (26)–(28) may be conceived as an outer-sphere

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* Recently, unambiguous evidence was provided for electron transfer from coordinated Cl^- to Pt^{IV}, and the formation of $[Pt^{III}Cl_5^{2-}]$ and Cl in the primary step of the photolysis of $PtCl_6^{2-}$ [165].

electron transfer from arene to the excited complex V or VI with subsequent extrusion of Cl^- anion (see Scheme 5 for complex V). It should be noted that in the
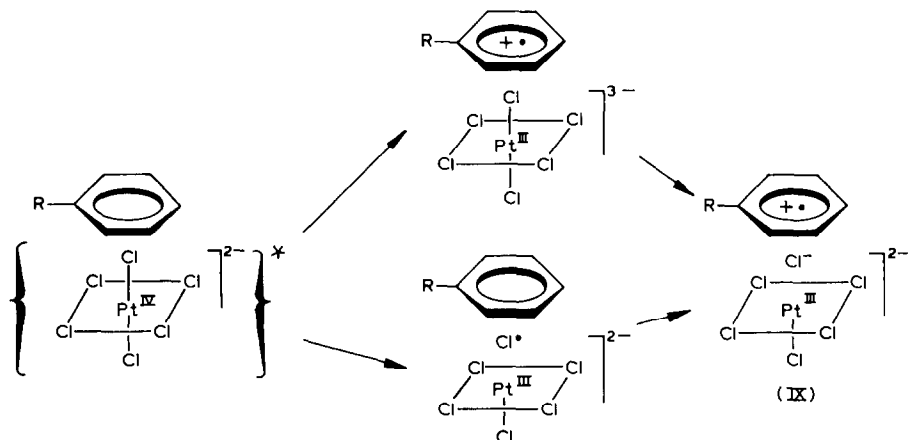
SCHEME 5

solid at 77 K, the mutual movement of an arene and Cl^- (or $Cl^{\cdot}$) is restricted and the ESR spectrum of the irradiated frozen solution may be due to structure IX in Scheme 5.

An alternative mechanism of ion-radical pair formation involves the extrusion of Cl^- anion and the formation of a π-complex of $[PtCl_5^-]^*$ with an arene molecule, accompanied with inner-sphere electron transfer:

$$\left[PtCl_6^{2-}\right]^* \rightarrow \left[PtCl_5^-\right]^* + Cl^- \tag{29}$$

$$[PtCl_5^-]^* + ArH \rightarrow [ArH]^{+\cdot}\left[Pt^{III}Cl_5^{2-}\right] \tag{30}$$

This mechanism, however, is certainly not valid for the solid state process of platinum(III) complex generation.

Subsequent transformations of the anion-radical pairs can be conceived as follows. First, they can decompose to afford the initial compounds:

$$[ArH]^{+\cdot}\left[Pt^{III}Cl_5^{2-}\right] \xrightarrow{k_5} ArH + Pt^{IV}Cl_5^- \tag{31}$$

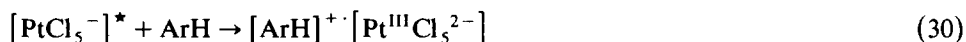$$[ArH]^{+\cdot}\left[Pt^{III}Cl_4(H_2O)^-\right] \xrightarrow{k_5} ArH + Pt^{IV}Cl_4(H_2O) \tag{32}$$

$$PtCl_5^- + Cl^- \rightarrow PtCl_6^{2-} \tag{33}$$

$$PtCl_5^- + H_2O \rightarrow PtCl_5(H_2O)^- \tag{34}$$

$$PtCl_4(H_2O) + Cl^- \rightarrow PtCl_5(H_2O)^- \tag{35}$$
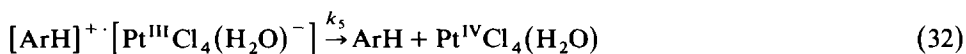
The second route is the collapse of the ion-radical pair to produce the Wheland complex III:

$$[ArH]^{+\cdot}\left[Pt^{III}Cl_5^{2-}\right] \xrightarrow{k_6} (Ar^+H)-Pt^{IV}Cl_5^{2-} \tag{36}$$
$$\text{(III)}$$

$$[ArH]^{+\cdot}\left[Pt^{III}Cl_4(H_2O)^-\right] \xrightarrow{k_6} (Ar^+H)-Pt^{IV}Cl_4(H_2O)^- \tag{37}$$
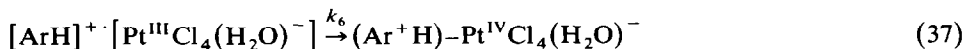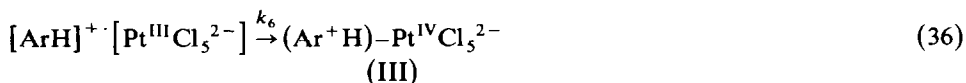
The substituent CH_3 or OCH_3 directs the entering platinum-containing moiety to the *para*-position (yield of para-isomer $\geqslant 95\%$).

Under the action of a base (i.e. CH_3COO^-), the Wheland complex gives the σ-aryl complex of platinum(IV):

$$(Ar^+H)-PtCl_5^{2-} \xrightarrow{k_7} \sigma\text{-ArPtCl}_5^{2-} + H^+ \tag{38}$$

$$(Ar^+H)-PtCl_4(H_2O)^- \xrightarrow{k_7} \sigma\text{-ArPtCl}_4(H_2O)^- + H^+ \tag{39}$$
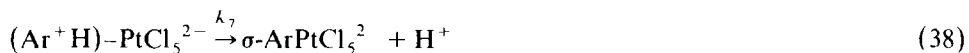
After chromatography on silica gel containing NH_3, complex II is obtained:

$$ArPtCl_5^{2-} + NH_3 \rightarrow ArPtCl_4(NH_3)^- + Cl^- \tag{40}$$

$$ArPtCl_4(H_2O)^- + NH_3 \rightarrow ArPtCl_4(NH_3)^- + H_2O \tag{41}$$

Kinetic analysis of Scheme 4 (including eqs. 23, 25, 27, 28, 32, 34, 35 and 37) in steady-state approximation leads to the following expression for the initial rate of reaction 20:

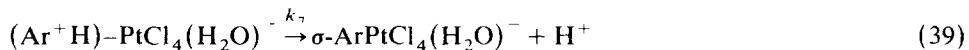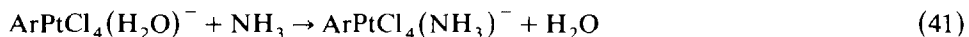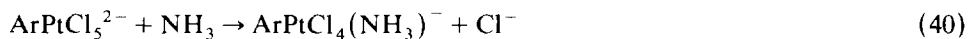$$W_0' = k_6([VII] + [VIII]) = \frac{k_4 k_6 [ArH]_0 \left(k_1 \left[PtCl_6^{2-} \right]_0 + k_2 \left[PtCl_5(H_2O)^- \right]_0 \right)}{(k_5 + k_6)(k_3 + k_4[ArH]_0)} \tag{42}$$

If $k_1 \simeq k_2$ and $k_5 \gg k_6$, eq. 42 is reduced to the following:

$$W_0' \simeq \frac{k_1 k_4 k_6 [ArH]_0}{k_5(k_3 + k_4[ArH]_0)} [Pt^{IV}]_0 \tag{43}$$

where $[Pt^{IV}]_0$ is the total initial concentration of H_2PtCl_6.

Equation 43 can serve to explain the weak dependence of the reaction rate on $[ArH]_0$ at high arene concentrations. To account for the observed character of the dependence of W_0' on the intensity of light I, it seems reasonable to assume that reactions 31 and 32 may proceed both thermally and under the action of light, so that

$$k_5 = k_5' + k_5''I \tag{44}$$

At low light intensities, $k_5' > k_5''I$, and the reaction rate increases linearly with I due to the linear increase of k_1. At high intensities, the second term in eq. 44 prevails, and the reaction rate becomes independent of I. The relatively small decrease of the reaction rate with increasing chloride ion concentration may be due to the higher reactivity of complexes containing water as a ligand (e.g. VI).

The reactions of organic compounds [62–65], and particularly arenes [66–79], with metal complexes involving an electron-transfer stage are widely known. The thermal reactions of arenes with Co^{III} [68,70,73,74,76], Mn^{III} [66,67], Pb^{IV} [69], Ce^{IV} [71,75,78] and Tl^{III} [72,77] were found to proceed via the formation of cation-radicals of arenes. In the last years, it has been suggested that the mechanisms of electrophilic and nucleophilic substitutions in organic compounds, and particularly in aromatics, involve an electron-transfer stage [80–93]. Electron-transfer processes in organic reactions, as well as the charge-transfer complexes and ion-radical salts formed in these reactions, are of great interest for organic chemistry and catalysis [94–98].

Although electron transfer is known to be induced by the action of light [99,100], so far only a few papers have been published dealing with the phototransfer of an electron from an arene to a metal complex or some other electron-deficient species. Kochi and co-workers [101] reported the isolation of an electron donor-acceptor complex, hexamethylbenzene-$Hg(OCOCF_3)_2$, in which irradiation of the charge-transfer absorption band induced electron transfer and ion-pair formation: $[(CH_3)_6C_6]^{+\cdot}$ $[Hg^I(OCOCF_3)_2^{-}]$. The first stage of the photochemical nitration of phenol by tetranitromethane is believed to involve photocatalysed electron-transfer within the donor-acceptor complex to form the phenol cation-radical and the tetranitromethane anion-radical pair [102]. Electron transfer was proposed to be the first stage of the photoinduced reactions of $PtCl_6^{2-}$ with various organic and organometallic compounds [18–22].

We believe that the photoinduced as well as the γ-induced reaction 20 is the first example of electrophilic substitution in aromatic compounds to take place through excitation of an electrophile (i.e. $PtCl_6^{2-}$). For a reaction of this type to take place (and to be observed), certain conditions must be fulfilled. The corresponding thermal reaction should be slow compared to the light-induced process. Light must excite the electrophile selectively and not the arene. Finally, the product of the reaction must be stable under the action of light. Thus, it is not easy to find an arene-electrophile system capable of electrophilic substitution via excitation of the electrophile. In contrast, examples of electrophilic substitution in aromatics induced by photoexcitation of an arene are rather numerous (hydrogen-deuterium and hydrogen-tritium exchange, deboronation, destannylation, nitration, acylation, ethoxycarbonylmethylation and the rearrangement of aromatic azoxy compounds) [103–106]. The following principal mechanisms were proposed for such electrophilic photosubstitutions [106–108]: $S_E1(Ar^\star)$, $S_E2(Ar^\star)$, and $S_{EA}(Ar^\star)$. For example, the $S_E2(Ar^\star)$ mechanism appears to be operating in photoinduced (λ 254 nm) aromatic cyanomethylation [109]. This reaction was proposed to involve initial excitation of the aromatic molecule, followed by electron transfer to chloro-acetonitrile: $ArH^\star + ClCH_2CN \rightarrow (ArH \cdots ClCH_2CN)^\star \rightarrow ([ArH]^+[ClCH_2CN^{-\cdot}])$ $\rightarrow ([ArH]^+[CH_2CN]^\cdot + Cl^- \rightarrow HAr^+CH_2CN \rightarrow ArCH_2CN + H^+$. Formally, this mechanism is similar to that of photoinduced platination of aromatics proposed in the present paper, the difference being in the nature of the species excited.

Finally, an alternative radical mechanism of the formation of the σ-aryl complex of platinum(IV) should not be excluded. This mechanism involves the formation of a Pt^{III} complex and $Cl^\cdot$ in the primary step of the photoreaction (see footnote on p. 138) and the subsequent reaction of $Cl^\cdot$ with the arene (possibly in a solvent cage) to produce HCl and the radical $Ar^\cdot$. Recombination of the latter with $Pt^{III}Cl_5^{2-}$ leads to the formation of the σ-aryl complex of platinum(IV).

Comparison of the thermal and photoinduced reactions

As is evident from the results of the two preceding sections, the thermal and photochemical (as well as γ-induced) reactions of σ-aryl platinum(IV) complex formation have certain important features in common. In fact, the reaction rates of these two types of reactions correlate with the σ^+ constants of the substituents in the benzene ring, the values of ρ^+ being practically identical ($\rho^+ \simeq -1.5$). In both cases, a small kinetic isotope effect is observed ($k_H/k_D \simeq 2$–3). Both heating [3] and light irradiation of a solution of $PtCl_6^{2-}$ with naphthalene or biphenyl in acetic acid leads

to the formation of a green complex which may possibly be identified as an intermediate Wheland-type zwitterionic complex. Thus, it can be concluded that the thermal and photoinduced reactions proceed via certain common stages. These stages appear to be Wheland complex (III) formation and transformation of this complex into σ-aryl complex (I).

The two types of reactions differ, however, concerning the *para-meta* isomerisation of platinated monosubstituted benzenes. While in the case of the thermal reaction intensive isomerisation is observed in acidic media at 70–100 °C, no isomerisation occurs in the course of the photochemical and γ-induced reactions (temperatures were ca. 20 °C for the former and ca. 50 °C for the latter). High temperature (> 70 °C) appears to be necessary for the isomerisation process to take place.

Figure 34 shows a schematic energy profile of the reactions under consideration which reflects certain characteristic features of the thermal and photochemical processes. When the kinetic schemes of both types of reactions as well as the diagram in Fig. 34 are considered, the question whether or not the thermal reaction involves the formation of the intermediate $[ArH]^+ [Pt^{III}]$ pair, as is assumed in the case of the photochemical reaction, arises. A variety of thermal reactions of electrophilic substitution in aromatic compounds are now believed to proceed via electron transfer from an arene molecule to an electrophile to afford ion-radical pairs [80,81,87–90]. Although no direct experimental data which unambiguously suggests the formation of platinum(III) complexes and aromatic cation-radicals in the thermal reaction of arene with $PtCl_6^{2-}$ have been obtained, such an assumption
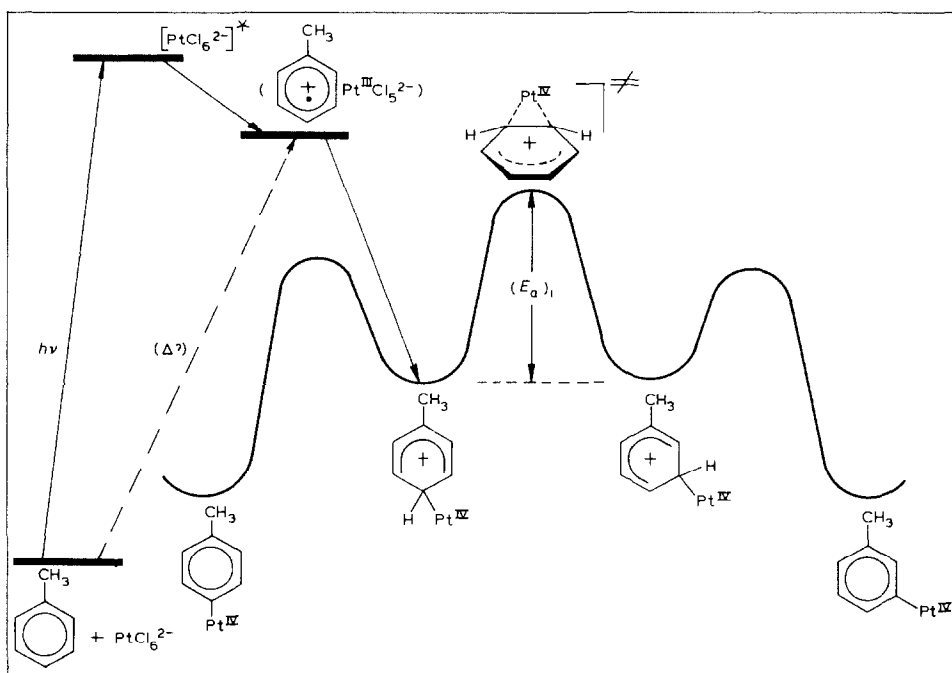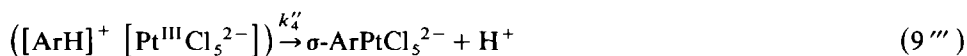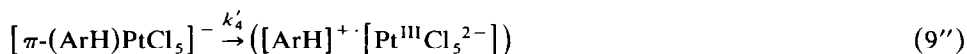

Fig. 34. Schematic energy profile for the thermal and photochemical reactions of σ-aryl platinum(IV) complex formation and isomerisation.

does not contradict the observed kinetics of these reactions. Indeed, in this case, stage (9) of the thermal reaction Scheme 1 should be replaced by

$$[\pi\text{-}(ArH)PtCl_5]^- \overset{k'_4}{\to} ([ArH]^{+\cdot}[Pt^{III}Cl_5^{2-}]) \qquad (9'')$$

$$([ArH]^+[Pt^{III}Cl_5^{2-}]) \overset{k''_4}{\to} \sigma\text{-}ArPtCl_5^{2-} + H^+ \qquad (9''')$$

If we take into account the fact that the formation of an ion-radical pair is believed to be the rate-determining step in electrophilic substitution [90] and use the steady-state approximation for the concentration of $([ArH]^+[Pt^{III}Cl_5^{2-}])$, the expression for the rate of the thermal reaction will preserve the form of 11 with k_4 being replaced by k'_4.

Indirect evidence in favour of the existence of the electron-transfer stage in question is the observed trend of the dependence of the relative rates V_0 of the thermal reaction on the ionization potentials I or oxidation potentials E_{ox}^o of the arenes (Fig. 35).

It is convenient to label the proposed mechanism of the photoinduced as well as the γ-induced reaction as the $S_E2e.t.$ mechanism (electrophilic substitution with a crucial associative step involving an electron-transfer step). The first part of this notation refers to the well-known S_E2 mechanism of substitution in aromatics involving Wheland complex formation as a crucial associative stage. The additional index 'e.t.' indicates that the reaction proceeds via an important stage of electron
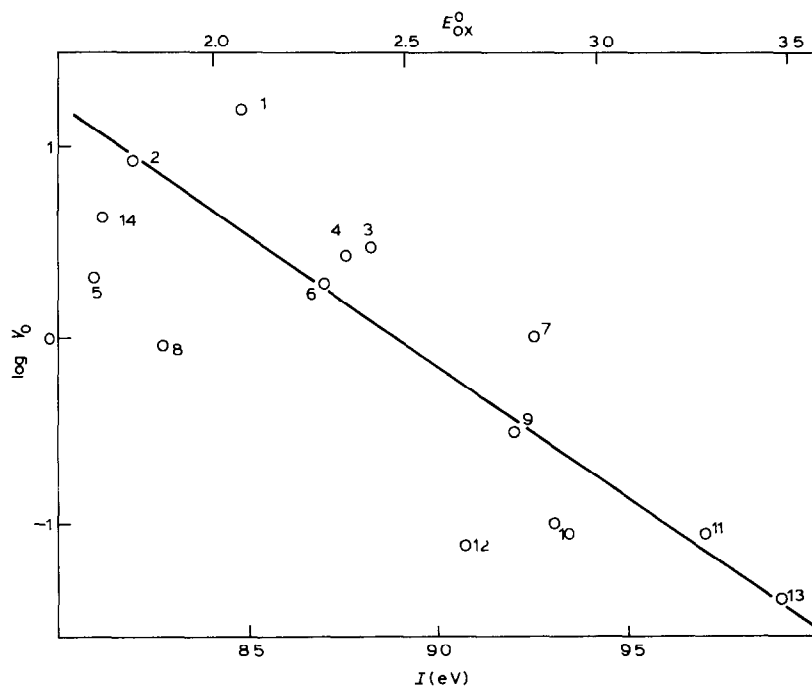

Fig. 35. Plot of logarithm of V_0 for thermal reaction (1)-(2) vs. the ionization potential I and the oxidation potential E_{ox}^o (see Table 1; 14 = naphthalene).

transfer. The electron-transfer stage might possibly turn out to be involved in each thermal electrophilic substitution reaction in aromatics (see, for examples [80,81,87–90]); in this case the label 'e.t.' should be omitted.

Comparison of the reaction of $PtCl_6^{2-}$ with arenes with other metallation reactions

Metallation reactions of aromatics which afford more or less stable σ-aryl compounds of metals are known mainly for non-transition heavy metals: mercury(II) [110], thallium(III) [111], and lead(IV) [112]. All these reactions proceed in organic acid solvents. In 1931, Kharasch and Isbell discovered the auration reaction of aromatics in aprotic media [113]. The ion $AuCl_4^-$ appeared to metallate electron-rich aromatics (phenol, *p*-dimethoxybenzene, naphthalene) in acetic acid [114], but the resulting σ-complexes were rather unstable and could not be fully characterized. In 1979, we found that another transition metal, viz. platinum(IV), in the form $PtCl_6^{2-}$, reacts readily with aromatics in organic acids [1,2]. This reaction appeared to be analogous to mercuration, thallation and plumbation, and all the heavy metals capable of arene metallation arrange in the sequence shown in Fig. 36. All these metals belong to the same row of the Periodic Table. The valence of the metal active in the metallation decreases from IV to II on going from platinum to mercury, and then increases to IV again on going to lead.

Selected parameters characterizing the metallation reactions are summarized in Table 4. Data for palladation reactions [115–118] are also given although inter-

TABLE 4

ARENE METALLATION REACTIONS

	Pt^{IV}	Au^{III}	Hg^{II}	Tl^{III}	Pb^{IV}	Pd^{II}
Metallation	[1,2]	[113,114]	[119]	[120,121]	[122–124]	[115,116]
$\rho(\sigma)$	-3.0[a]	?	?	-12.8[b] [125]	?	?
$\rho^+(\sigma^+)$	-1.5[a]	?	-6.3[e] [126]	-6.9[c] [126] -7.4[b] [125] -8.3[c] [127]	-9[f] [129]	-0.4[h] [115] -0.7[i] [135] -1.4[j] [136]
k_H/k_D	3.0 (B)[a] 2.3 (T)[a]	?	5.6 (B)[e] [128] 7.0 (T)[e] [128]	5.0 (T)[b] [125] 4.3 (B)[c] [127]	4.5 (A) [130]	4.5 (B)[k] [137] 3.5 (T)[k] [137] 5.1 (B)[j] [138]
$S_f = \log(f_p^{Me}/f_m^{Me})$	1.25[a]	?	1.3[e] [126]	1.5[c] [126] 1.8[d] [132]	1.7[f] [129] 2.0[g] [129]	-0.03[i] [135]
Transarylation	[7,14]	?	[139,140]	[133]	? [131]	absent
o-m-p-Isomerisation	[26]	?	[134]	[126]	?	absent [135]
Acceleration by light	[15]	absent[a] ? [101]		?	?	absent[a]

[a] This work. [b] Tl(OCOCF$_3$)$_3$ in CF$_3$COOH. [c] Tl(OCOCH$_3$)$_3$ in CF$_3$COOH. [d] Tl(OCOCH$_3$)$_3$ in CH$_3$COOH/H$_2$O/H$_2$SO$_4$. [e] Hg(OCOCF$_3$)$_2$ in CF$_3$COOH. [f] Pb(OCOCF$_3$)$_4$ in CF$_3$COOH. [g] Pb(OCOCH$_3$)$_4$ in CHCl$_2$COOH. [h] PdCl$_2$ in CH$_3$COOH, oxidative coupling. [i] Pd(OCOCH$_3$)$_2$ in CH$_3$COOH, oxidative coupling. [j] Pd(OCOCH$_3$)$_2$ in CH$_3$COOH/dioxane, olefins arylations. [k] Pd(OCOCH$_3$)$_2$ in CH$_3$COOH, acetoxylation; A = anisole; B = benzene; T = toluene.

mediate σ-aryl complexes of palladium(II) are unstable. In some aspects, the reaction of $PtCl_6^{2-}$ with arenes resembles palladation, the σ-aryl complexes of platinum(IV) serving as stable models of transient σ-aryl complexes of palladium(II) [7,9,10,13]. The σ-aryl complexes of gold(III) are rather unstable and the parameters of the auration reaction are not yet available. Mercuration, thallation and plumbation are the most carefully studied reactions.

Table 4 shows that the values ρ^+ and k_H/k_D for the thermal reaction of $PtCl_6^{2-}$ are somewhat lower than those for the reactions of mercury(II), thallium(III) and lead(IV). The selectivities S_f of all the reactions (except for palladation) are between 1 and 2, but in the case of the reaction of $PtCl_6^{2-}$ the partial rate factor for metallation to the *meta*-position of toluene is lower than that in the other cases. This leads to a value of 1.04 for a in the Brown equation [135,141]:

$$\log f_p^{Me} = aS_f \tag{45}$$

which is somewhat lower than the value 1.31 obtained for many other electrophilic substitution reactions [135] (see also [142]).

It is interesting to note that the thermal reactions of arenes with $Pb(OCOCH_3)_4$ [143] or thallium(III) compounds [72,77], as well as the photoinduced reaction of hexamethylbenzene with $Hg(OCOCF_3)_2$ [101], afford ESR spectra, which were attributed to cation-radicals of the aromatics. Thus, the metallation reactions under discussion (both thermal and photochemical) may be assumed [90] to proceed via the electron-transfer stage, followed by recombination of the cation-radical and the metal ion to produce the Wheland complex.

There are some other similar features which characterized the reactivity of platinum(IV) complexes on the one hand and that of mercury(II), thallium(III), and lead(IV) compounds on the other: the instability of π-complexes with arenes or olefins as well as hydrides, the oxidation reactions (dimerization, acetoxylation, chlorination etc.) of arenes (see, for example, [48,65,144,145]) or olefins (see, for example, [146–151]) by all these metal compounds.

As far as we know, in addition to the reactions of platinum(IV) and gold(III) complexes only one example of direct (intermolecular) electrophilic metallation of aromatics by a transition metal complex, i.e. octaethylporphirinatorhodium(III) chloride, is known [152]. Intermolecular metallations of aromatics via oxidative-ad-
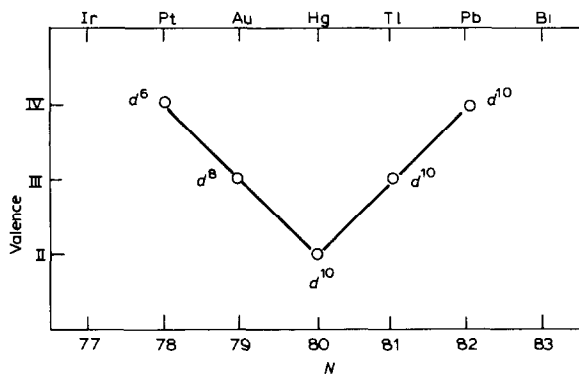

Fig. 36. Metal ions known to metallate arenes electrophilically to afford stable σ-aryl compounds.

dition have also been reported (see, for example, [153–155]). In contrast to inter-molecular metallations, many cyclometallation reactions are known [156,157].

Reaction of PtCl₆²⁻ with arylmercurials

Reactions of aryl-group transfer from one metal to another are well known for various non-transition and transition metals (see, for example, [64,140,158–160]). Earlier we found that $PtCl_6^{2-}$ induces cleavage of the bond between aryl and mercury, tin, lead or boron to afford σ-aryl complexes of platinum(IV) [7–11]. Here we report a study of the kinetics and mechanism of the reaction of $PtCl_6^{2-}$ with mercury diaryls in acetone. The low solubility of monoaryl mercurials, as well as that of aryl derivatives of tin and lead, did not allow the kinetics of the reactions with these compounds to be studied.

The reaction of Na_2PtCl_6 with mercury diphenyl and mercury di-(p-tolyl) in acetone was studied in aqueous acetone solutions at different temperatures (Fig. 37):

$$Ar_2Hg + PtCl_6^{2-} \rightarrow \sigma\text{-}ArPtCl_5^{2-} \qquad (46)$$
$$(I)$$
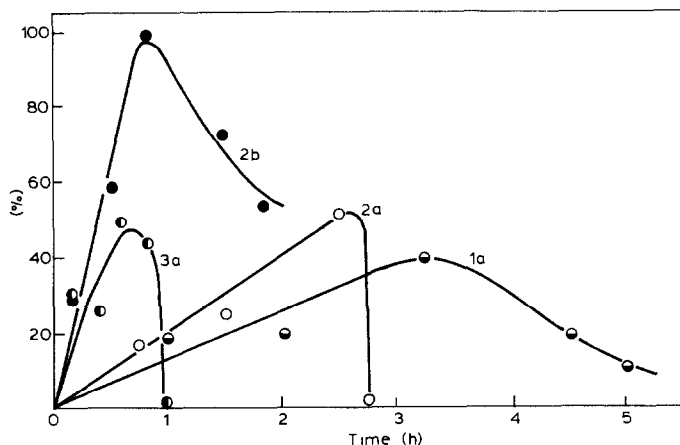

Fig. 37. Plots of the yield of complex II in the reaction of $Na_2PtCl_6 \cdot 6H_2O$ (0.025 M) with Ph_2Hg (0.125 M) (a) and (p-$CH_3C_6H_4)_2Hg$ (0.125 M) (b) at 34.5°C (1); 42°C (2) and 53.5°C (3).
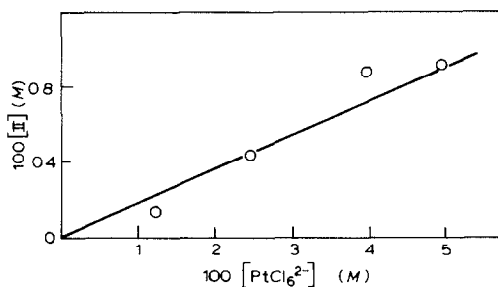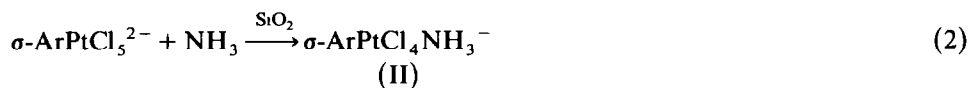

Fig. 38. Plot of the concentration of complex II formed in reaction (46-2) of Na_2PtCl_6 with Ph_2Hg (0.125 M) in acetone vs. [Na_2PtCl_6] (42°C, 60 min reaction time.)

$$\sigma\text{-ArPtCl}_5{}^{2-} + NH_3 \xrightarrow{\text{SiO}_2} \sigma\text{-ArPtCl}_4NH_3{}^{-} \qquad (2)$$
$$(II)$$

The estimated values of ρ and ρ^+, using two points only, are -3.5 and -2.0, respectively. The reaction is first order in $PtCl_6{}^{2-}$ (Fig. 38) and zero order in $(C_6H_5)Hg$ (Fig. 39). The rate of the reaction decreases with increasing concentration of LiCl added (Fig. 40).

The reaction of $PtCl_6{}^{2-}$ with diaryl mercury appears to be the electrophilic substitution of a mercury atom and is similar to the halogen demercuration reaction of Ar_2Hg or ArHgBr with $Hal_3{}^{-}$ [140,161–163]. Scheme 6 can be proposed for the mechanism of reaction 46.

SCHEME 6

$$PtCl_6{}^{2-} \rightleftharpoons PtCl_5{}^{-} + Cl^{-} \qquad (47)$$

$$PtCl_5(H_2O)^{-} \rightleftharpoons PtCl_5{}^{-} + H_2O \qquad (48)$$

$$Ar_2Hg + PtCl_5{}^{-} \rightleftharpoons Ar_2Hg\cdot PtCl_5{}^{-} \qquad (49)$$
$$(X)$$

$$Ar_2Hg\cdot PtCl_5{}^{-} \rightleftharpoons \sigma\text{-ArPtCl}_5{}^{-} + ArHg^{+} \qquad (50)$$

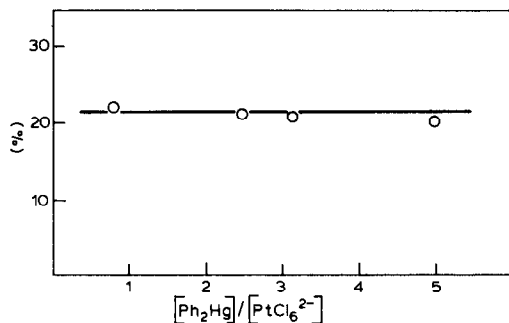Fig. 39. Plot of the yield of complex II formed in reaction (46-2) of Na_2PtCl_6 (0.025 M) with Ph_2Hg vs. Ph_2Hg concentration (with respect to Pt^{IV}) (42°C, 60 min reaction time).
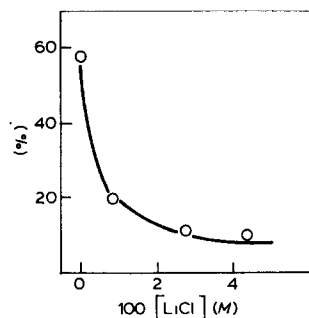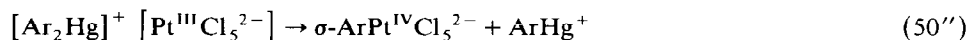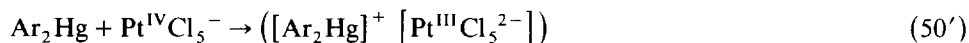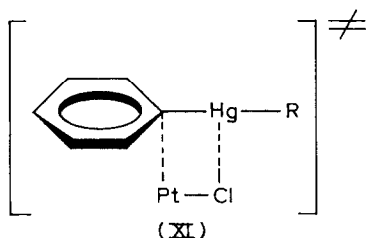

Fig. 40. Plot of the yield of complex II formed in reaction (46-2) of Na_2PtCl_6 (0.025 M) with $(p\text{-CH}_3C_6H_4)_2Hg$ (0.125 M) in aqueous acetone vs. LiCl added (42°C, 32 min reaction time).

$$ArHg^+ + Cl^- \rightleftharpoons ArHgCl \tag{51}$$

Stage 50 may proceed via the conventional four-centre transition-state XI (the $S_E i$ mechanism) or the S_E l.e.t. mechanism, (50′) and (50″), may operate (see [19]):

$$(XI)$$

$$Ar_2Hg + Pt^{IV}Cl_5^- \rightarrow \left([Ar_2Hg]^+ \left[Pt^{III}Cl_5^{2-} \right] \right) \tag{50'}$$

$$[Ar_2Hg]^+ \left[Pt^{III}Cl_5^{2-} \right] \rightarrow \sigma\text{-}ArPt^{IV}Cl_5^{2-} + ArHg^+ \tag{50''}$$

The $S_E i$ mechanism is perhaps less probable because of the large steric hindrance of the ion $PtCl_5^-$. The mechanism involving electron transfer has an analogy in the literature [64,140]. The electron-transfer stage was proposed to be involved in the reaction of Ar_2Hg with $Ph_3C^+X^-$ [164]. Electron transfer is the most probable for the reaction of $PtCl_6^{2-}$ with tetraaryl derivatives of tin and lead [7], where steric hindrance is very large. It should be noted that a light-irradiated frozen solution of $PtCl_6^{2-}$ and Ph_2Hg in CH_3COOH exhibited ESR spectra containing signals due to a platinum(III) complex and organic radicals (or cation-radicals) at $g \simeq 2.0$.

The qualitative explanation for the observed dependences in the terms of Scheme 6 is analogous to that in the case of the thermal and photoinduced reactions of $PtCl_6^{2-}$ with arenes. Quantitative analysis, however, reveals certain discrepancies, possibly due to the fact that in reality the reaction scheme is more complicated, involving, for example, the formation of complexes of mercury compounds with chloride anion.

Experimental

All the reactions were carried out in air. Photochemical reactions were carried out in quartz or glass cylindrical vessels cooled with water and irradiated with the light of a high-pressure mercury lamp (1000 W) under vigorous stirring. Aliquots of the reaction solutions after extraction of an arene with hexane or chloroform were evaporated under reduced pressure and the residue was chromatographed on a silica gel column containing 1–2 mg of NH_3 per 1 g of SiO_2. Concentrations of the complexes formed were measured spectrophotometrically (Specord UV-VIS), using absorption in the visible region. The relative rates in the competitive reactions were determined by ^1H NMR spectroscopy (Bruker SXP-4-100 spectrometer) of the mixtures of complexes formed.

Appendix

Kinetic analysis of Scheme 2

To make the subsequent calculations more compact, we will introduce the

following notations:

$\sigma_p = [\text{ }p\text{-Pt–Ar}]$; $\sigma_m = [m\text{-Pt–Ar}]$; $\sigma = \sigma_p + \sigma_m$;

$\kappa_p = k_{\text{obsd}}^P [\text{ArH}]_0$; $\kappa_m = k_{\text{obsd}}^m [\text{ArH}]_0$; $\kappa = \kappa_p + \kappa_m$;

$M = [\text{Pt}^{\text{IV}}]$; $t = \text{time}$

We will also assume that $[\text{ArH}]_0 \gg M$.

Then the rate of σ-complex formation is:

$$W = \frac{d\sigma}{dt} = \frac{dM}{dt} = \kappa M,$$

so, that

$$M = M_0 e^{-\kappa t}; \quad \sigma = M_0 \left(1 - e^{-\kappa t}\right).$$

The rate of *para*-isomer formation is given by

$$W_p = \frac{d\sigma_p}{dt} = \kappa_p M - k_{\text{1}}\sigma_p + \tfrac{1}{2}k_{\text{1}}\sigma_m.$$

Replacing σ_m by $\sigma - \sigma_p$ and σ by $M_0(1 - e^{-\kappa t})$, we obtain:

$$\frac{d\sigma_p}{dt} = \tfrac{1}{2}k_{\text{1}}M_0 + \left(\kappa_p - \tfrac{1}{2}k_{\text{1}}\right)M_0 e^{-\kappa t} - \tfrac{3}{2}k_{\text{i}}\sigma_p \tag{A-1}$$

The general solution of eq. (A-1) may be presented as

$$\sigma_p = \frac{M_0}{3} + Ae^{-\kappa t} + Be^{-(3/2)k_{\text{1}}t} \tag{A-2}$$

At $t \to 0$, $\sigma_p \to 0$, so that

$$A + B = -\frac{M_0}{3} \tag{A-3}$$

Substitution of eq. (A-2) into (A-3) gives

$$-A\kappa e^{-\kappa t} - \tfrac{3}{2}k_{\text{1}}Be^{-(3/2)k_{\text{1}}t} = \tfrac{1}{2}k_{\text{1}}M_0 + \left(\kappa_p - \tfrac{1}{2}k_{\text{i}}\right)M_0 e^{-\kappa t}$$

$$- \tfrac{3}{2}k_{\text{1}}\frac{M_0}{3} - \tfrac{3}{2}k_{\text{1}}Ae^{-\kappa t} - \tfrac{3}{2}k_{\text{1}}Be^{-(3/2)k_{\text{1}}t},$$

or

$$-A\kappa = \left(\kappa_p - \tfrac{1}{2}k_{\text{1}}\right)M_0 - \tfrac{3}{2}k_{\text{i}}A,$$

so that

$$A = \frac{2\kappa_p - k_{\text{i}}}{3k_{\text{i}} - 2\kappa}M_0;$$

$$B = -\frac{M_0}{3} - A = \frac{6\kappa_p - 2\kappa}{3(2\kappa - 3k_{\text{i}})}M_0$$

Then eq. (A-2) is reduced to

$$\sigma_p = \frac{M_0}{3} - \frac{M_0}{3}e^{-\kappa t} + \left(A + \frac{M_0}{3}\right)e^{-\kappa t} + Be^{-(3/2)k_{\text{1}}t}$$

$$= \frac{M_0}{3} \left(1 - e^{-\kappa t} \right) + B \left(e^{-(3/2)k_1 t} - e^{-\kappa t} \right)$$

$$= \tfrac{1}{3}\sigma + \frac{6\kappa_p - 2\kappa}{3(2\kappa - 3k_1)} \left(e^{-(3/2)k_1 t} - e^{-\kappa t} \right).$$

The relative yield of the *para*-isomer is then given by the equation

$$Y_p = \frac{\sigma_p}{\sigma} = \tfrac{1}{3} + \frac{6\kappa_p - 2\kappa}{3(2\kappa - 3k_1)} \left(e^{-(3/2)k_1 t} - e^{-\kappa t} \right)$$

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