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OXIDATION OF PLATINUM(II) COMPLEXES BY TETRACHLOROAURATE(III) IONS IN THE PRESENCE OF TETRAETHYLAMMONIUM CHLORIDE

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Very little attention has so far been devoted to the rates and mechanisms of oxidation of platinum(II) complexes. The work carried out in this field has been confined to the study of the oxidation of some charged platinum(II) complexes by platinum(IV) complexes [1], or, occasionally by other oxidizing reagents [2]. Moreover, only very few kinetic investigations have been carried out on the oxidation of uncharged platinum(II) complexes although they have been extensively studied with respect to nucleophilic substitution reactions [2—5]. As part of a systematic investigation on the oxidation reactions of this kind of complex we report here the kinetics of the oxidation of some platinum(II) complexes ([Pt(bipy)Cl_2], *trans*-[Pt$(AsEt_3)_2Cl_2$], *trans*-[Pt$(PEt_3)_2$(R)Cl], R = Cl, C_6H_5, *m*-FC_6H_4, *p*-FC_6H_4, *p*-ClC_6H_4, *p*-$CH_3OC_6H_4$) in acetonitrile by tetrachloroaurate(III) ions in the presence of tetraethylammonium chloride. A constant ionic strength (0.1 *M*) has been obtained by adding to the reacting mixtures the appropriate amount of tetraethylammonium perchlorate which behaves as a strong electrolyte in acetonitrile, as well as the corresponding chloride [6, 7].

EXPERIMENTAL

Materials

Platinum(II) and platinum(IV) complexes were usually prepared following the literature methods [8—12]. *trans*-[Pt$(PEt_3)_2$(R)Cl_3] (R = C_6H_5, *m*-FC_6H_4, *p*-FC_6H_4, *p*-ClC_6H_4, *p*-$CH_3OC_6H_4$) were prepared by oxidation of the platinum(II) complexes in CCl_4 with chlorine. [Pt(bipy)Cl_4] has been prepared by oxidizing the corresponding platinum(II) complex in DMF with either Cl_2 or hydrogen peroxide and hydrogen chloride and recovered by addition of water to the reaction mixture. Hydrogen tetrachloroaurate(III) was used as 3-hydrate. Acetonitrile was purified by standard methods [13].

Preparation of the reaction mixtures, stoichiometry of the reactions and evaluation of the reaction rates

Stock solutions of platinum(II) complexes, Et_4NCl, Et_4NClO_4 and $HAuCl_4.3H_2O$ were prepared by weight. The concentration of gold(III) was then accurately determined spectrophotometrically, the molar extinction coefficient of tetrachloroaurate(III) in acetonitrile at 322 nm being known [14]. The reactions were started by mixing the appropriate volumes of thermostatted solutions of the reactants directly in 1 cm silica cells maintained in the thermostatted cell compartment of an Optica CF4R recording spectrophotometer. The reference cell contained tetraethylammonium salts in the same concentration as that present in the reacting mixture, whereas gold(III) was some 10^{-3} *M* less concentrated. The concentration of Et_4NCl was varied in the range 1.00×10^{-1} *M* — 2.00×10^{-2} *M*. The concentration ranges of $HAuCl_4$ explored were as follows: $3.20 \times 10^{-3} - 1.60 \times 10^{-4}$ *M* for *trans*-$[Pt(PEt_3)_2(m\text{-}FC_6H_4)Cl]$; $3.14 \times 10^{-3} - 2.85 \times 10^{-4}$ *M* for *trans*-$[Pt(PEt_3)_2(p\text{-}ClC_6H_4)Cl]$ and *trans*-$[Pt(AsEt_3)_2Cl_2]$; $3.06 \times 10^{-3} - 7.65 \times 10^{-4}$ *M* for *trans*-$[Pt(PEt_3)_2Cl_2]$; $3.06 \times 10^{-3} - 3.20 \times 10^{-4}$ *M* for the other complexes. The concentration of the complexes was usually at least 10 times lower than that of $HAuCl_4$. At suitable time intervals the spectrum

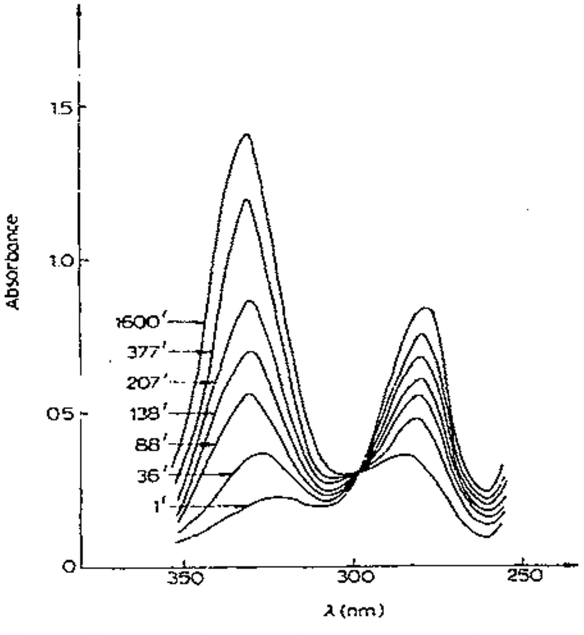


Fig. 1. Spectral changes during the reaction in acetonitrile at 50° C of *trans*-$[Pt(AsEt_3)_2Cl_2]$ (5.4×10^{-5} *M*) with $HAuCl_4$ (3.14×10^{-4} *M*) in the presence of Et_4NCl (1.00×10^{-1} *M*).

of the reacting mixture was scanned over the range of wavelength 400—250 nm, where high changes of absorbance were found to occur during the reaction together with one or more isosbestic points (e.g. Fig. 1). The position of such isosbestic points and the detailed analysis of the spectra of the reaction mixtures showed that all the reactions examined follow the stoichiometric eq. (1). The composition of the gold(I) complex was inferred on the basis of the known stability of $AuCl_2^-$ in acetonitrile [14]. The reactions were found to go to completion, in the pseudo-first-order conditions employed, following a pseudo-first-order rate law. The rates were found to be unaffected by addition of small amounts of water (up to 1%) to the reacting mixture. The pseudo-first-order rate constants, k_{obs}, were determined from the slope of log $(D_t - D_\infty)$ or log $(D_\infty - D_t)$ against time, where D_t and D_∞ are the absorbances of the reacting mixture at time t and at the end of the reaction at a given wavelength. In some cases, when the reactions were extremely slow and decomposition of the reaction products was possible, the value of D_∞ was not derived experimentally and a value derived from faster reactions was used.

RESULTS AND DISCUSSION

All the platinum(II) complexes have been found to undergo oxidation to platinum(IV) by tetrachloroaurate(III) ions, in the presence of chloride ions, according to eq. (1) in which the uncharged ligands, L, maintain their mutual

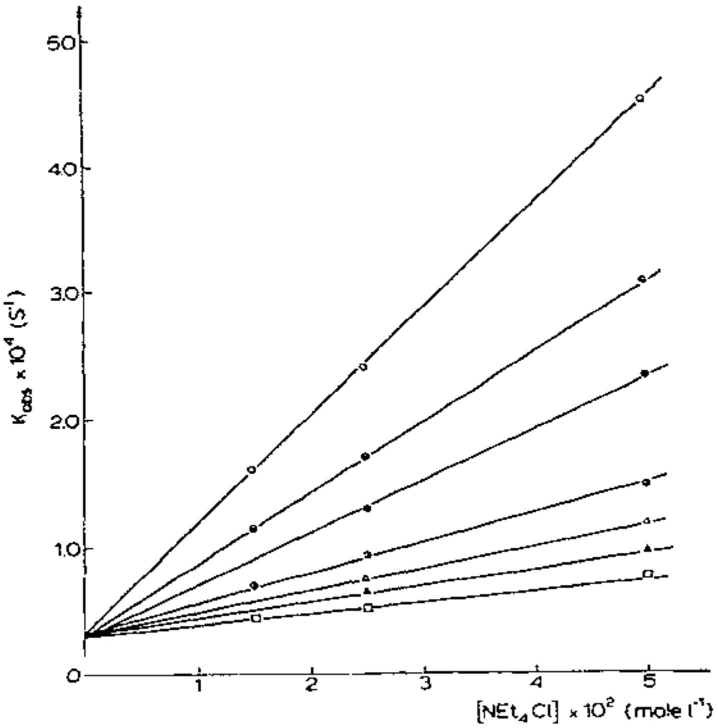
$$[PtL_2(R)Cl] + AuCl_4^- \rightarrow [PtL_2(R)Cl_3] + AuCl_2^- \qquad (1)$$

position also in the reaction products. No elementary gold was formed in our experimental conditions (see experimental section). The reactions were found to go to completion and obeyed a two term rate law. A third order rate term, first order with respect to platinum(II), to tetrachloroaurate(III) and to chloride, was found to operate in each case examined (e.g. Figs. 2 and 3). The form of the other rate term which appears in the overall rate law equation is different for the various platinum(II) complexes considered. In the case of $[Pt(bipy)Cl_2]$ or *trans*-$[Pt(AsEt_3)_2Cl_2]$ such a rate term is independent of either gold(III) or chloride concentrations, as shown by the fact that the straight lines obtained on plotting k_{obs} towards chloride or gold(III) concentrations for several series of kinetic runs (e.g. Figs. 2(a) and 2(c)) give the same intercept. Therefore, the overall rate law operating in these cases is

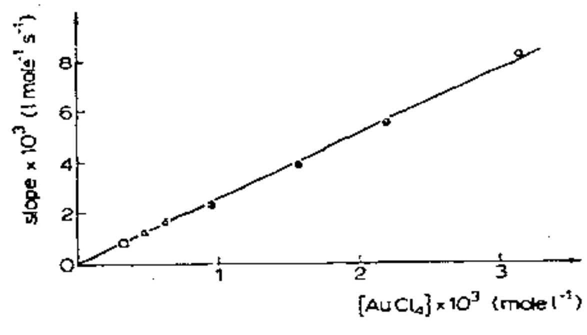
$$\text{rate} = k_3[PtL_2(R)Cl][AuCl_4^-][Cl^-] + k_s[PtL_2(R)Cl] \qquad (2)$$

When the triethylphosphine—platinum(II) derivatives are used the rate term under discussion is found to depend also on the gold(III) concentration, as shown by the occurrence of different intercepts obtained by plotting k_{obs} against chloride concentration for a series of kinetic runs carried out using different gold(III) concentrations (e.g. Fig. 3(a)). Moreover, in these cases the

k_{obs} is not linearly dependent on the gold(III) concentration (see, for example, Fig. 3(c)). Such behaviour cannot be related to changes of acidity arising from changes in the concentration of hydrogen tetrachloroaurate(III). In fact, changes of hydrogen ion concentration are not seen to affect the rates. Thus, the value of k_{obs} for the oxidation of *trans*-[Pt(PEt$_3$)$_2$(m-FC$_6$H$_4$)Cl] at 35°C in the presence of Cl$^-$ (0.1 M) and AuCl$_4^-$ (1.80 × 10^{-3} M) is 1.43 × 10^{-4} s^{-1} for [H$^+$] = 1.80 × 10^{-3} M; 1.44 × 10^{-4} s^{-1} for [H$^+$] = 4.38 × 10^{-3} M;



(a)



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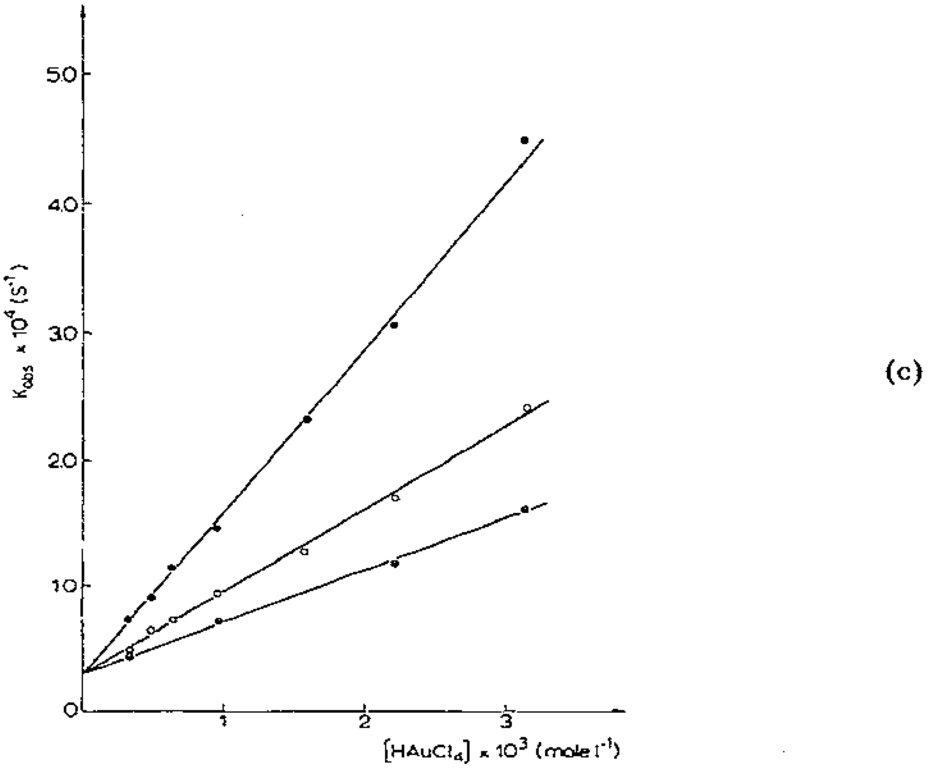


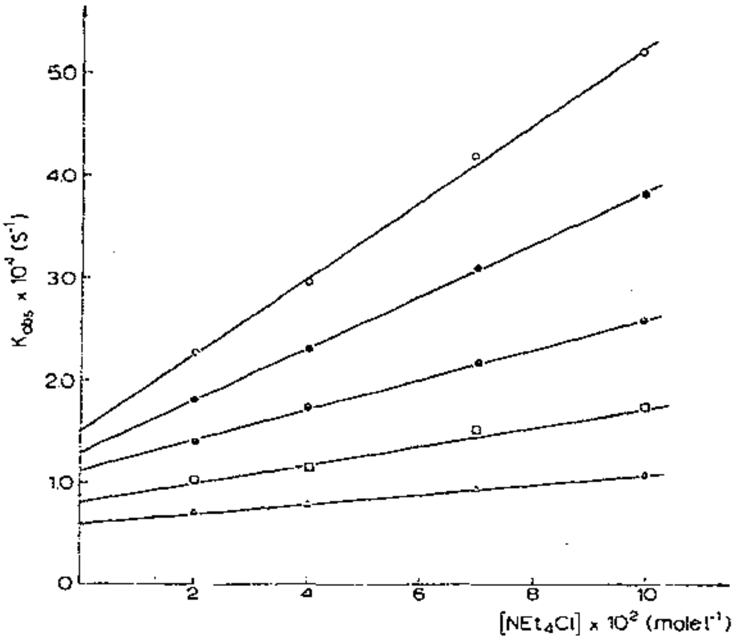
Fig. 2. Oxidation of *trans*-[Pt(AsEt$_3$)$_2$Cl$_2$] at 50° C. (a) Plots of k_{obs} vs. the concentration of Et$_4$NCl. [HAuCl$_4$] = 3.14×10^{-3} *M* (○), 2.20×10^{-3} *M* (◒), 1.57×10^{-3} *M* (●), 9.40×10^{-4} *M* (◐), 6.28×10^{-4} *M* (△), 4.70×10^{-4} *M* (▲), 3.14×10^{-4} *M* (□).
(b) Plot of the slopes in Fig. 2a vs the concentration of HAuCl$_4$.
(c) Plots of k_{obs} vs the concentration of HAuCl$_4$. [Et$_4$NCl] = 5.00×10^{-2} *M* (●), 2.50×10^{-2} *M* (○), 1.50×10^{-2} *M* (◒).

1.39×10^{-4} s^{-1} for [H$^+$] = 6.95×10^{-3} *M*; 1.37×10^{-4} s^{-1} for [H$^+$] = 1.28×10^{-2} *M*. The kinetic results for the oxidation of the phosphine—platinum(II) complexes are best fitted by eqn. (3) which becomes equal to rate law (2) when [AuCl$_4^-$] $\gg k$.

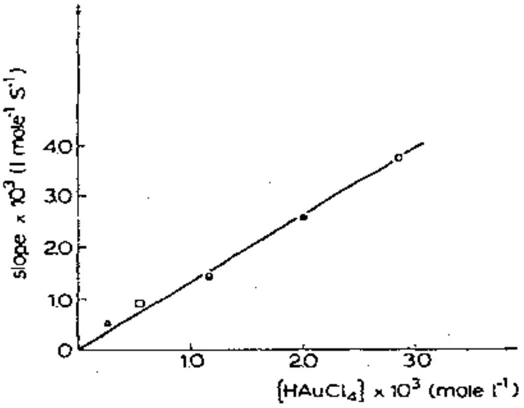
$$\text{rate} = k_3[\text{PtL}_2(\text{R})\text{Cl}][\text{AuCl}_4^-][\text{Cl}^-] + \frac{k_s[\text{PtL}_2(\text{R})\text{Cl}][\text{AuCl}_4^-]}{k + [\text{AuCl}_4^-]} \qquad (3)$$

Values of k_3, k_s and k obtained in the single cases are reported in Table 1.

Rate laws (2) and (3) suggest that the oxidation of platinum(II) complexes by tetrachloroaurate(III) ions follows two reaction pathways. We think that the rate term k_s is the consequence of a solvolytic reaction, involving the starting complex, of the type which is known to operate in the nucleophilic substitution reactions of platinum(II) complexes. Of course, a solvent assisted reaction path is expected to operate only when the oxidant is able to react with the solvent-complex intermediate with a rate sufficient to compete with the chloride ion. According to the above interpretation we have found a value of k_s for the substitution reaction of *trans*-[Pt(AsEt$_3$)$_2$Cl$_2$] with bromide very close to the value obtained for oxidation with gold(III) (see Table 1). We have also obtained some approximate values of k_s from nucleo-



(a)



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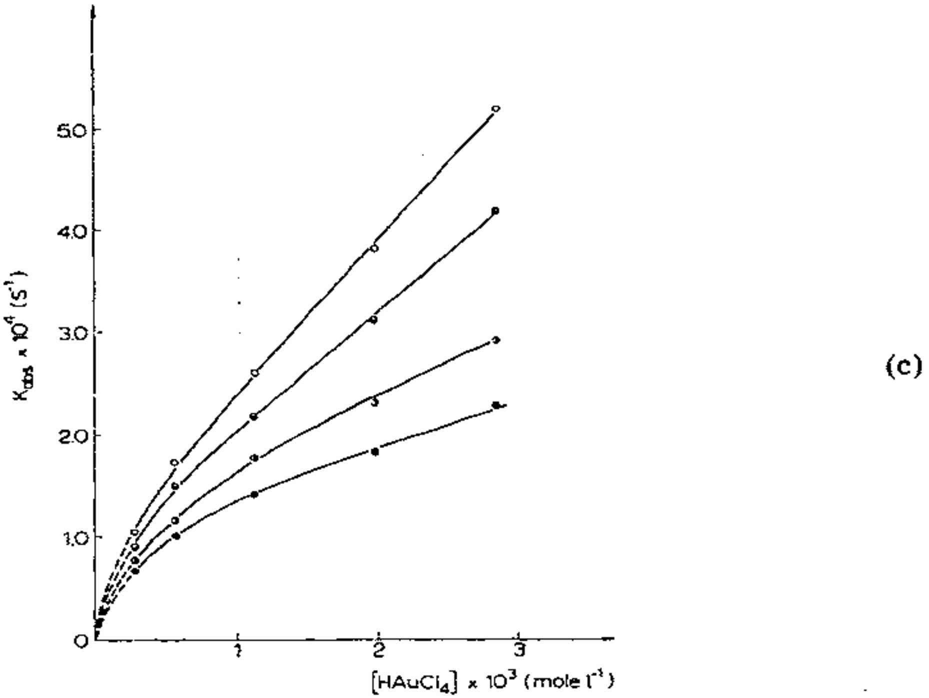


Fig. 3. Oxidation of *trans*-[Pt(PEt$_3$)$_2$(*p*-ClC$_6$H$_4$)Cl] at 50° C. (a) Plots of k_{obs} vs the concentration of Et$_4$NCl. [HAuCl$_4$] = 2.85×10^{-3} *M* (○), 2.00×10^{-3} *M* (●), 1.14×10^{-3} *M* (◓), 5.70×10^{-4} *M* (□), 2.85×10^{-4} *M* (Δ).
(b) Plot of the slopes of Fig. 3a vs the concentration of HAuCl$_4$.
(c) Plots of k_{obs} vs the concentration of HAuCl$_4$. [Et$_4$NCl] = 1.00×10^{-1} *M* (○), 7.00×10^{-2} *M* (◓), 4.00×10^{-2} *M* (◐), 2.00×10^{-2} *M* (●).

philic substitution reactions of *trans*-[Pt(PEt$_3$)$_2$(R)Cl] (R = aryl group). In these cases the reactions do not go to completion even when good nucleophiles such as iodide or thiourea are used in relatively high concentrations (up to 5×10^{-2} *M* for I$^-$) and the evaluation of k_{obs} was made by assuming that the reactions go to completion and using only data relevant to the early stages of the reactions.

The third order rate term, related to k_3, implies an activated complex for the rate determining step containing a molecule of platinum(II) complex, one tetrachloroaurate(III) ion and one chloride ion. Thus, the overall reaction mechanism for the reactions under consideration can be schematized as follows:

$$[\mathrm{PtL_2(R)Cl}] + \mathrm{AuCl_4^-} + \mathrm{Cl^-} \xrightarrow{k_3} [\mathrm{PtL_2(R)Cl_3}] + \mathrm{AuCl_2^-} + \mathrm{Cl^-} \tag{4a}$$

$$[\mathrm{PtL_2(R)Cl}] + \mathrm{S} \underset{k_{-s}}{\overset{k_s}{\rightleftharpoons}} [\mathrm{PtL_2(R)\,(S)}]^+ + \mathrm{Cl^-} \tag{4b}$$

$$[\mathrm{PtL_2(R)(S)}]^+ + \mathrm{AuCl_4^-} + \mathrm{Cl^-} \xrightarrow{k_3'} [\mathrm{PtL_2(R)Cl_3}] + \mathrm{AuCl_2^-} + \mathrm{S} \tag{4c}$$

TABLE 1

Rate constants and activation parameters[a] for the redox reaction: $[PtL_2(R)Cl] + AuCl_4^- \xrightarrow{Cl^-} [PtL_2(R)Cl_3] + AuCl_2^-$ in acetonitrile

Complex	T(°C)	k_3 (l^2mole^{-2}s^{-1})	$\Delta H_3^{\ne}$ (kcal mole^{-1})	$\Delta S_3^{\ne}$ (cal K^{-1} mole^{-1})	k_s (s^{-1})	k_s[b] (s^{-1})	k (mole L^{-1})
$[Pt(bipy)Cl_2]$	50	3.30	7.8	−32	$<1 \times 10^{-6}$	—	—
	35	1.74			~0	—	—
trans-$[Pt(AsEt_3)_2Cl_2]$	50	2.64	8.6	−30	3.2×10^{-5}	3.0×10^{-5}	—
	35	1.31			1.0×10^{-5}	7.5×10^{-5}	—
trans-$[Pt(PEt_3)_2Cl_2]$	50	10^{-1} [c]	—	—	—	—	—
trans-$[Pt(PEt_3)_2(C_6H_5)Cl]$	50	7.60×10^{-1}	8.5	−33	2.6×10^{-4}	—	1.4×10^{-3}
	35	3.80×10^{-1}			1.3×10^{-4}	1.5×10^{-4}	2.8×10^{-3}
trans-$[Pt(PEt_3)_2(p\text{-}CH_3OC_6H_4)Cl]$	50	1.06	9.7	−30	2.8×10^{-4}	—	1.4×10^{-3}
	35	4.83×10^{-1}			1.9×10^{-4}	1.4×10^{-4}	2.3×10^{-3}
trans-$[Pt(PEt_3)_2(p\text{-}ClC_6H_4)Cl]$	50	1.32	8.5	−32	1.7×10^{-4}	—	6.0×10^{-4}
	35	6.60×10^{-1}			1.0×10^{-4}	1.3×10^{-4}	1.1×10^{-3}
trans-$[Pt(PEt_3)_2(p\text{-}FC_6H_4)Cl]$	50	1.27	8.3	−33	2.2×10^{-4}	—	8.8×10^{-4}
	35	6.45×10^{-1}			1.1×10^{-4}	—	1.3×10^{-3}
trans-$[Pt(PEt_3)_2(m\text{-}FC_6H_4)Cl]$	50	1.07	8.5	−33	1.7×10^{-4}	—	1.1×10^{-3}
	35	5.35×10^{-1}			9.0×10^{-5}	9.0×10^{-5}	8.8×10^{-4}

[a] Errors: $k_3 \pm 3\%$; $k_s \pm 10\%$; $k \pm 10\%$; $\Delta H_3^{\ne} \pm 1$ kcal mole^{-1}; $\Delta S_3^{\ne} \pm 3$ cal K^{-1}mole^{-1}.

[b] Data from substitution reactions.

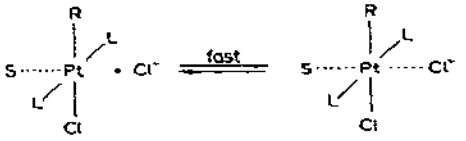
[c] ± 10%.

where eqns. (4b) and (4c) account for the solvent-assisted reaction path. The related rate law, derived by using the stationary state model, is

$$\text{rate} = k_3[\mathrm{PtL_2(R)Cl}][\mathrm{AuCl_4^-}][\mathrm{Cl^-}] + \frac{k_s[\mathrm{PtL_2(R)Cl}][\mathrm{AuCl_4^-}]}{k_{-s}/k'_3 + [\mathrm{AuCl_4^-}]} \tag{5}$$

Equation (5) has the same form as that found experimentally with $k = k_{-s}/k'_3$. It may be noticed that the actual occurrence of rate law (2) or (3) will depend upon the value of k_{-s}/k'_3 and, therefore, also upon the reactivity of chloride towards the solvent-complex intermediate. Thus, the reason why the aryl derivatives exhibit rate law (3) is to be regarded as a consequence of the high reactivity of chloride towards such intermediates.

The third order pathway exhibits relatively low values of activation enthalpy, the order of magnitude being that normally found in redox reactions involving a bridge mechanism. On the other hand, it also exhibits high negative values of the entropy of activation which are probably due to the formation of a fairly rigid bridged activated complex. Therefore, it may be thought that redox step (4a) (and probably also step (4c)) involves the formation of a bridged intermediate with a chloride ion simultaneously bonded to platinum(II) and to gold(III). At least three different redox mechanisms involving a bridged intermediate can account for redox step (4a). First of all it may be noticed that a third order rate term of the same form as that under discussion has also been found to operate in the oxidation of platinum(II) derivatives by platinum(IV) complexes in the presence of chloride ions [1]. In these kind of reactions the reaction mechanism is thought to involve a fast reversible formation of a five-coordinate adduct between platinum(II) and free chloride, followed by an atom-transfer redox step between the platinum(IV) complex and such a five-coordinate adduct. A similar mechanism could operate even when the oxidizing agent is $\mathrm{AuCl_4^-}$. In such a case the detailed mechanism* would be as follows:



(6a)

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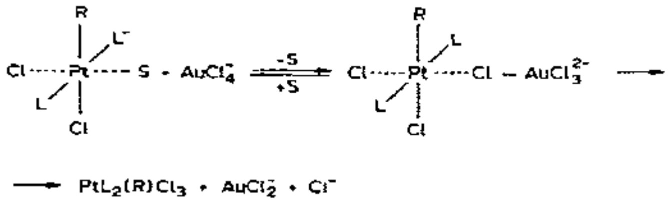
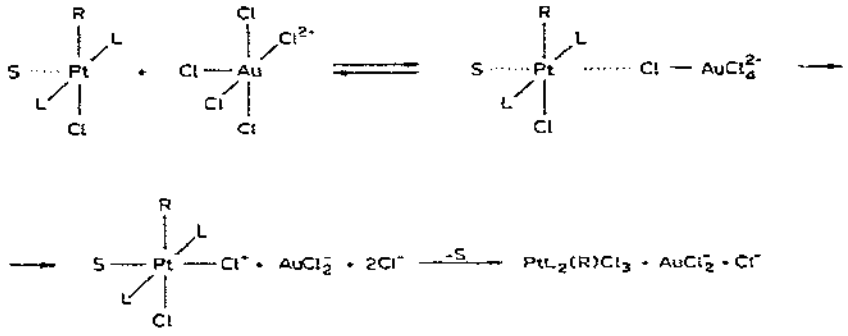
[*] A similar mechanism would also explain the redox step (4c) related to the solvent-assisted pathway, provided the redox step is followed by a fast substitution of the solvent molecule by a chloride ion.



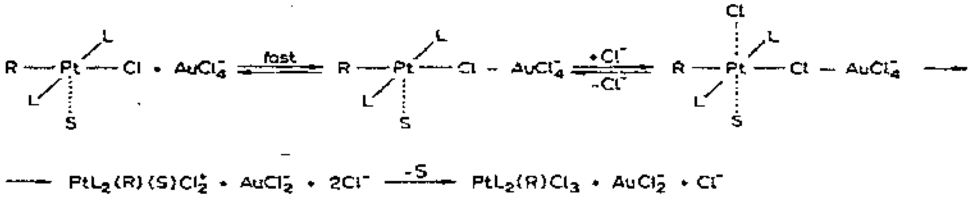
(6b)

An alternative redox mechanism, which takes into account the well known tendency of gold(III) to attain five-coordination [15,16], would involve the preliminary formation of a five-coordinate gold(III), AuCl$_5^{2-}$, which would then interact with the initial platinum(II) complex according to the following mechanism



(7a)

Finally, a redox mechanism which cannot be differentiated from the previous ones on the basis of the rate law alone, is one which implies an attack of AuCl$_4^-$ on a chloride bonded to the starting platinum(II) complex as a first reversible step, followed by a fast nucleophilic attack of chloride on the platinum(II) atom before the slow redox step



(8)

The reactivity towards direct oxidation, related to k_3, of the complexes examined is found to be a function of both the charged and uncharged ligands bonded to platinum(II) (see Table 1). We think that changes in the free energy of these reactions accompanying changes of the ligands bonded to platinum are among the most important factors which give rise to the observed reactivity trend. It is a rather general observation that the free energies of activation of redox reactions involving very similar systems [17,18] are lower, and thus the reactions are faster, when these are thermodynamically more favourable. Thus, one can expect that the reactivity order will be parallel with the thermodynamic ease of platinum(II) to be oxidized to platinum(IV). According to this hypothesis preliminary studies have shown that *cis*-[Pt(PEt$_3$)$_2$Cl$_2$] undergoes oxidation by $AuCl_4^-$ much more slowly than the *trans* isomer which is expected to exhibit a lower oxidation potential [19]. Thus, the reactivity order $AsEt_3 > PEt_3$ would be the consequence of a greater stabilizing influence on the higher oxidation state of a given central metal atom exhibited by tertiary arsines with respect to tertiary phosphines [20—22]. In agreement with the above considerations a reverse order of reactivity, i.e. $AsEt_3 < PEt_3$, has been previously found in the reduction of the related chlorocomplexes of platinum(IV) by several reducing agents [2]. Finally, the higher reactivity exhibited by triethylphosphine-complexes when R = aryl group with respect to R = Cl, can be tentatively assigned to the stronger σ-donor ability of Ar^- with respect to Cl^-, which would lead to an increased electron density on platinum(II) which consequently would lose electrons more easily. On the other hand, the negligible kinetic effect exhibited by the substituents in the aromatic ring is an indication that only strong changes in the basicity of the ligands will lead to appreciable changes of reactivity.

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