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THE KINETICS OF THE REDUCTION OF PLATINUM(IV) COMPLEXES BY FERROCENE IN HYDROXYLIC SOLVENTS

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A INTRODUCTION

The reduction reactions of platinum(IV) complexes have been extensively examined in the last few years[1–6] The work carried out in this field has been mainly concerned with redox reactions occurring by inner-sphere reaction mechanisms, whereas outer-sphere redox processes have only occasionally been investigated[7] In order to carry out a systematic study of the latter types of reaction, we have studied the reduction of platinum(IV) complexes by ferrocene, whose ability to act as reducing agent towards inorganic compounds is already known[8] Ferrocene is expected to favour outer-sphere redox mechanisms, because of its inertness to substitution and saturation of its coordination sphere Moreover, its solubility in most non-aqueous solvents makes possible the study of the reduction of several platinum(IV) complexes whose insolubility in water would prevent any investigation with other outer-sphere type reductants.

We have carried out an investigation of the kinetics of reduction of the complexes *trans*-$[PtL_2X_4]$ (L = $As(C_2H_5)_3$($AsEt_3$), $P(n\text{-}C_3H_7)_3$ (PPr_3), $P(C_2H_5)_3$ (PEt_3), $S(C_2H_5)_2$ (SEt_2), piperidine (pip), X = Cl, Br) by ferrocene in methanol, ethanol, 1-propanol, 2-propanol, 2-methyl-2-propanol, 1,2-ethanediol These platinum(IV) complexes were chosen because considerable information about their behaviour in redox reactions occurring through an inner-sphere redox mechanism is already available[3,9,10]

Ferrocene reacts quantitatively with the above-mentioned platinum(IV) complexes in all the solvents used, according to

$$trans\text{-}[PtL_2X_4] + 2\,Fe(C_5H_5)_2 \rightarrow trans\text{-}[PtL_2X_2] + 2\,Fe(C_5H_5)_2^{+} + 2\,X^{-} \qquad (1)$$

where L = $AsEt_3$, PPr_3, PEt_3, SEt_2, pip, X = Cl, Br

The reaction of all the platinum(IV) complexes under pseudo-first-order conditions obeys a pseudo-first-order rate law. The pseudo-first-order rate constants, k_{obs}, are linearly dependent upon the concentration of ferrocene, as shown by the examples reported in Fig. 1 Therefore, the rate law for the disappearance of platinum(IV) is given by the relationship

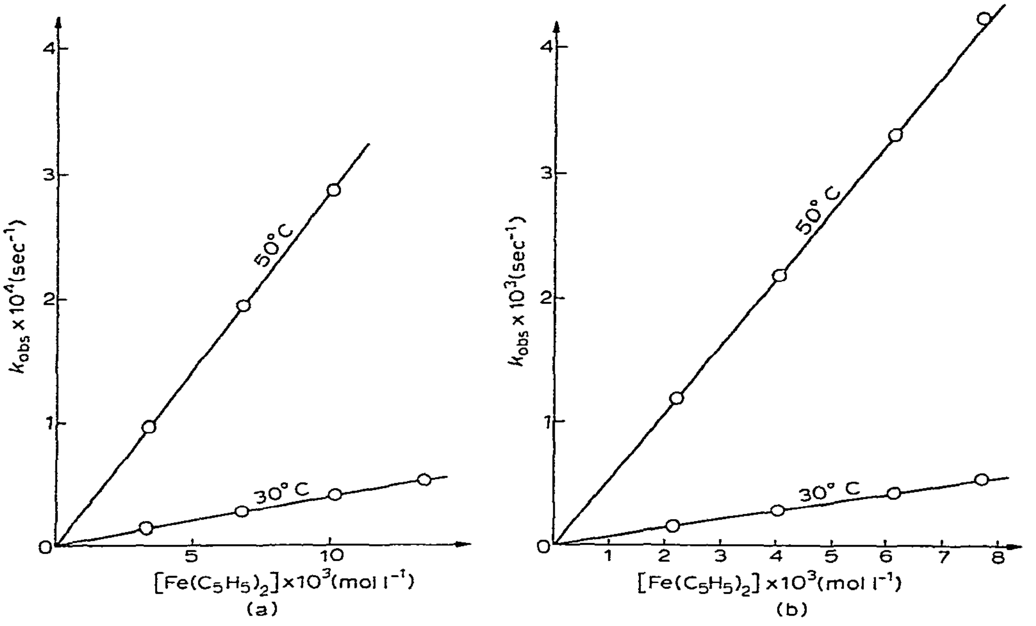


Fig 1 Pseudo-first-order rate constants k_{obs}, for the reduction of (a) *trans*-$[Pt(PPr_3)_2Br_4]$ in ethanol and (b) *trans*-$[Pt(PEt_3)_2Cl_4]$ in 1,2-ethanediol, as a function of ferrocene concentration

$$-\frac{d[Pt^{IV}]}{dt} = k[Pt^{IV}]\,[Fe(C_5H_5)_2] \tag{2}$$

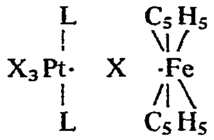
In Table I we have reported the values of the second-order rate constants, k, and the activation parameters.

The form of the rate law, together with the stoicheiometry of the reaction, is in agreement with a redox mechanism involving two monoelectronic redox steps, viz

$$Pt^{IV} + Fe^{II} \xrightarrow{slow} Pt^{III} + Fe^{III} \tag{3a}$$

$$Pt^{III} + Fe^{II} \xrightarrow{fast} Pt^{II} + Fe^{III} \tag{3b}$$

The first step is rate-determining and implies the formation of a platinum(III) intermediate. Platinum(III) intermediates in redox processes have already been invoked by several authors, and recently kinetic evidence of their occurrence has also been obtained[5,11,12] The possibility of a mechanism implying a bielectronic step, with the formation of an iron(IV) intermediate, is believed to be very unlikely On the basis of the inertness to substitution and saturation of coordination of ferrocene, it is very likely that the slow step involves an outer-sphere redox mechanism. In addition, an inner-sphere redox mechanism involving an activated complex such as I is expected to be prevented by the steric hindrance between the cyclopentadienyl rings of ferrocene and the large ligands L bonded *cis* with respect to the bridging halide



I

The reactivity of the platinum(IV) complexes with the same X is in the order $SEt_2 >$ pip $> PEt_3 > PPr_3 > AsEt_3$, in all the solvents employed The same sequence of reactivity has previously been found in methanol when these complexes are reduced by I^-, SCN^-, $SeCN^-$, $S_2O_3^{2-}$, $[Ni(diars)_2Y]^+$ (diars = *o*-phenylenebisdimethylarsine; Y = Cl, Br) through an inner-sphere redox mechanism[3,10,13] In these cases, the reactivities of the various *trans*-tetrachloro complexes at 40°C towards these reducing agents were found to obey the linear free energy relationship

$$\log k = r(X) + r_S \qquad (4)$$

where k is the second-order rate constant for the reduction of the substrate under consideration by a given reductant, $r(X)$ is the value of $\log k$ for the corresponding reaction of *trans*-$[Pt(PPr_3)_2Cl_4]$, selected as standard substrate, r_S is a constant whose value depends only upon the nature of the ligand L Now we find that the reactivity towards ferrocene of both *trans*-$[PtL_2Cl_4]$ and *trans*-$[PtL_2Br_4]$ is also related to the r_S values assigned to L (except for L = pip) Figure 2 shows that whatever the halide bonded to

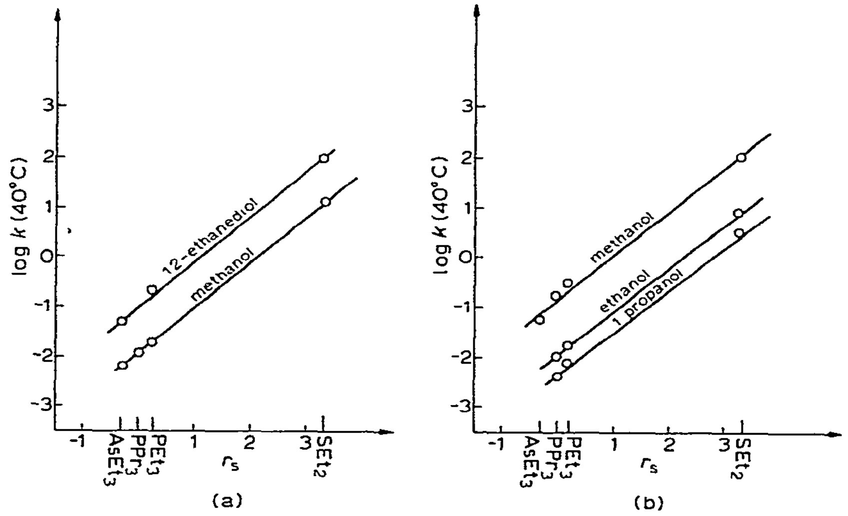


Fig. 2 Correlation between r_S and the values of $\log k$ for the reduction of (a) *trans*-$[PtL_2Cl_4]$ and (b) *trans*-$[PtL_2Br_4]$, at 40°C

TABLE 1

Second-order rate constants, k, and activation parameters[a] for the redox reaction *trans*-$[PtL_2X_4] + 2\ Fe(C_5H_5)_2 \rightarrow$ *trans* $[PtL_2X_2] + 2\ Fe(C_5H_5)_2^+ + 2\ X^-$

Solvent	Complex	Concn range of ferrocene (mole l^{-1})	Temp (°C)	k (l mole^{-1} sec^{-1})	ΔH^* (kcal mole^{-1})	ΔS^* (cal °K^{-1} mole^{-1})
Methanol	*trans* $[Pt(P(C_2H_5)_3)_2Br_4]$	$1\ 39 \times 10^{-2} - 3\ 47 \times 10^{-3}$	50	$6\ 28 \times 10^{-1}$		
			40	$2\ 73 \times 10^{-1}$	17 8	−5
			30	$9\ 50 \times 10^{-2}$		
	trans-$[Pt(P(n\ C_3H_7)_3)_2Br_4]$	$1\ 34 \times 10^{-2} - 3\ 34 \times 10^{-3}$	50	$4\ 60 \times 10^{-1}$		
			40	$1\ 85 \times 10^{-1}$	17 5	−6
			30	$7\ 25 \times 10^{-2}$		
	trans-$[Pt(As(C_2H_5)_3)_2Br_4]$	$1\ 34 \times 10^{-2} - 3\ 34 \times 10^{-3}$	50	$1\ 30 \times 10^{-1}$		
			40	$5\ 10 \times 10^{-2}$	18 8	−5
			30	$1\ 77 \times 10^{-2}$		
	trans-$[Pt(C_5H_{11}N)_2Br_4]$	$6\ 6 \times 10^{-3} - 1\ 67 \times 10^{-3}$	40	$1\ 76 \times 10^{1}$		
			20	2 68	16 5	0
	trans-$[Pt(S(C_2H_5)_2)_2Br_4]$	$1\ 00 \times 10^{-2} - 4\ 03 \times 10^{-3}$	32	$4\ 96 \times 10^{1}$		
			18	$1\ 35 \times 10^{1}$	15 8	+1
	trans-$[Pt(P(C_2H_5)_3)_2Cl_2Br_2]$	$1\ 34 \times 10^{-2} - 3\ 34 \times 10^{-3}$	50	$2\ 75 \times 10^{-1}$		
			30	$4\ 54 \times 10^{-2}$	16 9	−9
	trans-$[Pt(S(C_2H_5)_2)_2Cl_4]$	$1\ 34 \times 10^{-2} - 3\ 34 \times 10^{-3}$	40	$1\ 11 \times 10^{1}$		
			30	4 40	15 8	−3
			20	1 84		
	trans-$[Pt(P(C_2H_5)_3)_2Cl_4]$	$1\ 34 \times 10^{-2} - 3\ 34 \times 10^{-3}$	50	$5\ 20 \times 10^{-2}$		
			40	$1\ 95 \times 10^{-2}$	18 9	−6
			30	$7\ 00 \times 10^{-3}$		
	trans-$[Pt(P(n\text{-}C_3H_7)_3)_2Cl_4]$	$1\ 34 \times 10^{-2} - 3\ 34 \times 10^{-3}$	50	$3\ 00 \times 10^{-2}$		
			30	$4\ 50 \times 10^{-3}$	17 8	−11
	trans-$[Pt(As(C_2H_5)_3)_2Cl_4]$	$1\ 34 \times 10^{-2} - 3\ 34 \times 10^{-3}$	50	$1\ 59 \times 10^{-2}$		
			30	$1\ 95 \times 10^{-3}$	19 8	−6

Ethanol	*trans*-[Pt(P(C_2H_5)$_3$)$_2$Br$_4$]	1 34 x 10^{-2} – 3 34 x 10^{-3}	50	4 75 x 10^{-2}		
			30	5 95 x 10^{-3}	19 6	–4
	trans-[Pt(P(*n*-C_3H_7)$_3$)$_2$Br$_4$]	1 34 x 10^{-2} – 3 34 x 10^{-3}	50	2 86 x 10^{-2}		
			30	3 80 x 10^{-3}	19 0	–7
	trans-[Pt($C_5H_{11}N$)$_2$Br$_4$]	2 14 x 10^{-2} – 5 35 x 10^{-3}	40	3 35		
			20	4 40 x 10^{-1}	17 9	+1
	trans-[Pt(S(C_2H_5)$_2$)$_2$Br$_4$]	2 00 x 10^{-2} – 5 00 x 10^{-3}	40	7 40		
			20	1 00	17 6	+2
	trans-[Pt(S(C_2H_5)$_2$)$_2$Cl$_4$]	1 98 x 10^{-2} – 4 95 x 10^{-3}	50	1 85		
			30	3 00 x 10^{-1}	17 1	–6
1-Propanol	*trans*-[Pt(P(C_2H_5)$_3$)$_2$Br$_4$]	2 09 x 10^{-2} – 5 23 x 10^{-3}	50	1 69 x 10^{-2}		
			30	2 01 x 10^{-3}	20 1	–5
	trans-[Pt(P(*n*-C_3H_7)$_3$)$_2$Br$_4$]	2 05 x 10^{-2} – 5 14 x 10^{-3}	50	1 10 x 10^{-2}		
			30	1 35 x 10^{-3}	19 8	–6
	trans-[Pt($C_5H_{11}N$)$_2$Br$_4$]	2 21 x 10^{-2} – 5 53 x 10^{-3}	40	1 40		
			20	1 73 x 10^{-1}	18 4	+1
	trans-[Pt(S(C_2H_5)$_2$)$_2$Br$_4$]	2 02 x 10^{-2} – 5 05 x 10^{-3}	50	6 15		
			30	1 02	16 9	–3
	trans-[Pt(S(C_2H_5)$_2$)$_2$Cl$_4$]	2 02 x 10^{-2} – 5 05 x 10^{-3}	50	6 80 x 10^{-1}		
			30	1 06 x 10^{-1}	17 5	–5
2-Propanol	*trans*-[Pt(S(C_2H_5)$_2$)$_2$Br$_4$]	2 00 x 10^{-2} – 5 00 x 10^{-3}	50	1 62		
			30	2 88 x 10^{-1}	16 2	–8
	trans-[Pt(S(C_2H_5)$_2$)$_2$Cl$_4$]	2 57 x 10^{-2} – 6 44 x 10^{-3}	50	1 26 x 10^{-1}		
			30	1 92 x 10^{-2}	17 7	–8

TABLE 1 (continued)

Solvent	Complex	Concn range of ferrocene	Temp (°C)	k (l·mole^{-1} sec^{-1})	ΔH^* (kcal mole^{-1})	ΔS^* (cal °K^{-1}·mole^{-1})
2-Methyl-2-propanol	*trans*-[Pt(S(C$_2$H$_5$)$_2$)$_2$Br$_4$]	3 08 x 10^{-2} – 7.7 x 10^{-3}	50	2 90 x 10^{-1}		
			30	5 65 x 10^{-2}	15 3	–14
1,2-Ethanediol	*trans*-[Pt(P(C$_2$H$_5$)$_3$)$_2$Br$_4$]	7 64 x 10^{-3} – 2 14 x 10^{-3}	50	7 50		
			30	9 70 x 10^{-1}	19 3	+5
	trans-[Pt(P(C$_2$H$_5$)$_3$)$_2$Cl$_4$]	7 70 x 10^{-3} – 2 16 x 10^{-3}	50	5 50 x 10^{-1}		
			30	6 80 x 10^{-2}	19 8	+2
	trans-[Pt(S(C$_2$H$_5$)$_2$)$_2$Cl$_4$]	3 90 x 10^{-3} – 1 09 x 10^{-3}	40	1 00 x 10^{2}		
			20	1 27 x 10^{1}	18 2	+9
	trans-[Pt(As(C$_2$H$_5$)$_3$)$_2$Br$_4$]	7 40 x 10^{-3} – 2 10 x 10^{-3}	50	1 14		
			30	1 18 x 10^{-1}	21 4	+8
	trans-[Pt(As(C$_2$H$_5$)$_3$)$_2$Cl$_4$]	7 40 x 10^{-3} – 2 10 x 10^{-3}	50	1 49 x 10^{-1}		
			30	1 49 x 10^{-2}	21 8	+5

[a] The error is ± 3% in k, ± 1 kcal mole^{-1} in ΔH^*, ± 3 cal °K^{-1} mole^{-1} in ΔS^*

platinum(IV) and whatever solvent is used, the same linear relationship is obtained by plotting log k at 40°C against r_S Thus, changes of free energy of activation related to changes of L are unaffected by the halide bonded to platinum(IV), by the solvent used and by the mechanism operating This is in agreement with the hypothesis previously reported[3], according to which the change of reactivity towards reduction of *trans*-$[PtL_2X_4]$ complexes by changing L is related to its relative π-acceptor and σ-donor ability The slope of the lines of Fig 2 is 0 87 instead of 1, which would be expected on the basis of a relationship such as (4) It is not possible to discuss this point because it is not clear whether this difference in slope is reliable or due merely to some error in the assignment of the r_S value for L = SEt_2, which is most important in estimating the slope

The complex *trans*-$[Pt(pip)_2Br_4]$ always reacts faster than expected on the basis of the value of r_S assigned to piperidine (1.95) Although the reactivity in methanol of this complex does not deviate markedly from the expected value, wider discrepancies are encountered in ethanol and in 1-methanol In fact, the solvent effect in this case is different from that observed for all the other complexes, as shown in Fig 3 These anomalies are most likely related to the fact that piperidine is the only ligand in the series bearing an aminic proton, which can play a specific role in the solvation and stabilisation of the activated complex, possibly through hydrogen bonding with the solvent and with the

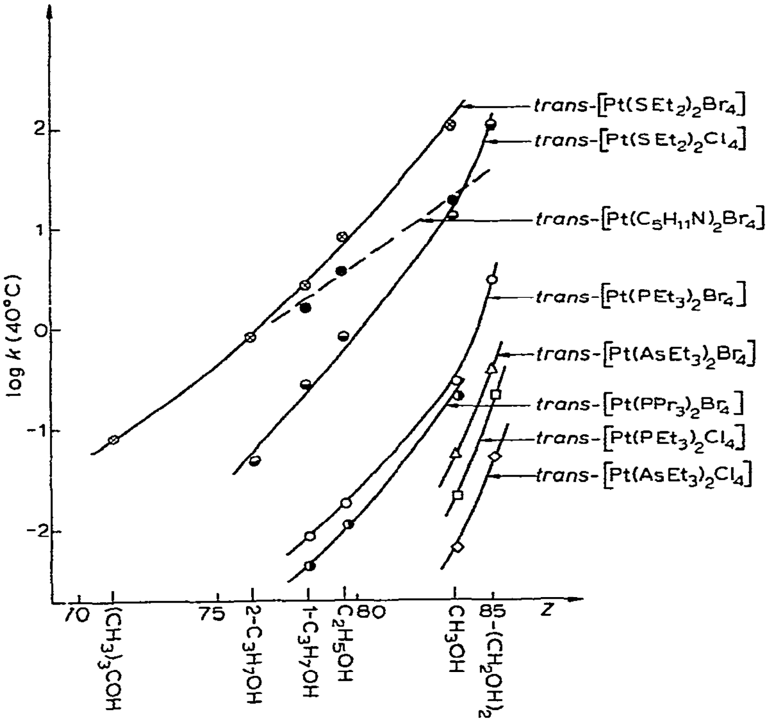


Fig 3 Correlation between the values of log k for the reduction of *trans*-$[PtL_2X_4]$ by ferrocene at 40°C and the polarity of the solvent, expressed in terms of Kosower's Z parameter

incoming reductant It must be pointed out that reactivities higher than expected on the basis of a linear relationship such as (4) have previously been found when complexes of the type *trans*-[Pt(NH_2R)$_2$$X_4$] react with thiosulphate[3] in methanolic solution

The tetrabromo complexes react 10–20 times faster than the corresponding tetrachloro complexes, independently of the ligand L and the solvent used Previous work on the same compounds showed that the bromo complexes react in methanol about 5000 times faster than the corresponding chloro complexes when the reductant was I^-, SCN^-, $SeCN^-$, $S_2O_3^{2-}$, $[Pt(diars)_2Y]^+$ (Y = Cl, Br, I)[3,9], and 50–200 times faster when the reductant was $[Ni(diars)_2Y]^+$ (Y = Cl, Br)[10] In these cases the reactions involve an inner-sphere redox mechanism, and the reactivity changes occurring by changing the halide depend on (i) the relatively easy formation of the bridging intermediate, which in turn depends in some way on the relative affinity of the reducing agent towards the bridging halide, and (ii) the relative stability of the oxidation products, which is related to the halides transferred On the other hand, when the reductant is ferrocene, no bond formation is believed to occur in going from the reactants to the activated complex, according to the mechanism proposed, and the oxidation product is always ferricinium, whatever the halide X bonded to platinum(IV). Here the reactivity change occurring by changing the halide can be assigned mainly to the lower deformation energy of *trans*-[PtL_2Br_4] with respect to *trans*-[PtL_2Cl_4] required to make these substrates available for the electron transfer★ The comparatively strongly higher reactivity observed in the inner-sphere reduction reactions of *trans*-[PtL_2Br_4] must be explained by the relative ease in making the bridged intermediate and by the relative stability of the oxidation products These factors have already been invoked to explain some kinetic features of the reduction of platinum(IV) complexes by inner-sphere reductants[10]. In this connection it is remarkable that although the bromo complexes are generally more reactive than the corresponding chloro complexes, we have found[14] that amino complexes of the type *trans*-[PtL_2Cl_4] in acid solution react with Fe^{2+} about 10 times faster than the corresponding *trans*-[PtL_2Br_4] In these cases the oxidation products are respectively $FeCl^{2+}$ and $FeBr^{2+}$, which quickly dissociate in solution The higher stability of $FeCl^{2+}$ is believed to be the most important factor contributing to the observed reactivity trend.

The reactivity towards ferrocene of the platinum(IV) complexes considered depends strongly on the solvent. Figure 3 shows that the reactivity increases with the polarity of the solvent, which has been expressed in terms of Kosower's Z values[15] Several theories on the solvent effect upon redox reactions occurring by an outer-sphere redox mechanism are known[16], but we cannot take advantage of them to explain quantitatively our results In fact, we should need to know the free energy changes of the elementary step (3a) with the solvent, which are not available and perhaps not even evaluable A qualitative explanation can however be offered. Bearing in mind that the reactants are uncharged, the trend of Fig 3 appears to be consistent with an activated complex in which separation of charges

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★Some change of reactivity must also be accounted for by the changes of driving force related to the reduction potentials of *trans*-[PtL_2X_4]

has occurred to some extent. In fact, a reaction involving separation of charges in the activated complex is expected to show a higher rate in more polar solvents Moreover, such a reaction path is also expected to show higher entropies of activation in more polar solvents[17] This expectation is in satisfactory agreement with our experimental results.

B EXPERIMENTAL SECTION

(i) Materials

Platinum(IV) complexes and ferrocene were prepared following the methods of the literature[3,13,18,19]

The solvents were purified following the standard methods[20]

(ii) Spectrophotometric studies

These were made by using either a Beckman DK2A or an Optica CF4R spectrophotometer The reactions were normally studied in situ, the silica cells being used as reaction vessels and constant temperature being maintained by circulating water from a thermostat through the cell holder A reference cell containing ferrocene in an equimolar amount to that of the reaction mixture was used in all cases

(a) Stoicheiometry of the reaction

Preliminary spectrophotometric measurements showed that the platinum(IV) complexes under investigation react with ferrocene in solution, yielding ferricinium as oxidised product The existence of isosbestic points either in the visible and/or in the UV region showed that no intermediates were formed in detectable amounts during the reaction Only in the case of *trans*-[$Pt(SEt_2)_2Br_4$] in 2-methyl-propanol did a second reaction occur However, this did not lead to formation of ferricinium, and was therefore subsequent to the redox step Ferricinium has been identified in solution from its absorbance spectrum in the region 450–700 nm[21] Moreover, a comparison of the absorbance spectrum of the reaction mixture at the end of the reaction with that of known solutions of ferricinium perchlorate showed that 2 g ions of ferricinium are always formed per mole of platinum(IV) reacted The reduction product, *trans*-[PtL_2X_2], has been identified by separation from the reaction mixture The general procedure was to react 10 ml platinum(IV) (1×10^{-3} mole 1^{-1}) with 2 ml ferrocene (1×10^{-2} mole $\cdot 1^{-1}$). At the end of the reaction both platinum(IV) and ferrocene had reacted quantitatively The reaction mixture was then treated with 20 ml ethyl ether and 20 ml water Th ethereal layer, containing only the platinum(II) complex, was dried over Na_2SO_4 and evaporated The residue was dissolved in methanol and identified by comparing its UV spectrum with that of known platinum(II) complexes The reduced product of the reaction of *trans*-[$Pt(SEt_2)_2Br_4$] in 2-methyl-2-propanol has not been isolated It has been identified as *trans*-[$Pt(SEt_2)_2Br_2$] from the isosbestic points present during the first stages of the reaction, their position being the same as that met in the other solvents

(b) Kinetics

Stock solutions of the reagents were prepared by weight, and appropriate volumes of the solutions, previously brought to the reaction temperature, were mixed in the spectrophotometric cell at the start of the reaction. At suitable time intervals the spectrum of the reacting mixture was scanned over 400–250 nm In the case of relatively fast reactions, the absorbance at a fixed wavelength in the UV region was recorded against time The reactions of *trans*-[Pt(SEt$_2$)$_2$Br$_4$] in methanol were followed by means of a stopped-flow apparatus The reactions were carried out by using concentrations of ferrocene at least 30 times higher than those of the starting platinum(IV) Table I reports the intervals of concentration of ferrocene explored in the single cases In such conditions the disappearance of platinum(IV) followed a pseudo-first-order rate law The pseudo-first-order rate constants, k_{obs}, were determined from the slope of the plots of log $(D_t - D_\infty)$ against time, where D_t and D_∞ are the absorbance of the reaction mixture at time t and at the end of the reaction, respectively The value of D_∞ for the reaction of *trans*-[Pt(SEt$_2$)$_2$Br$_4$] in 2-methyl-2-propanol was derived both by extrapolation methods[10] and from the known molar absorbance of ferricinium and *trans*-[Pt(SEt$_2$)$_2$Br$_2$], supposed to be the only products formed during the reaction The values of k_{obs} were then evaluated from the slope of log $(D_t - D_\infty)$ vs time for the first stages of the reaction.

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