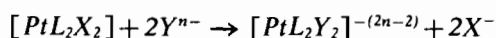


Redox Reaction Mechanisms of Platinum(IV) Complexes

A. Peloso, R. Ettore and G. Dolcetti

Received June 21, 1967

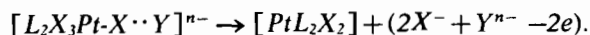
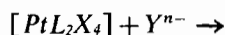
Kinetic investigations on redox reactions of platinum(IV) complexes $\text{trans-[Pt(PEt}_3)_2\text{Br}_4]$, and $\text{trans-[Pt(PPr}_3)_2\text{Br}_4]$ with SCN^- , I^- , SeCN^- and $\text{S}_2\text{O}_3^{2-}$, and of $\text{trans-[Pt(PEt}_3)_2\text{Cl}_4]$, $\text{trans-[Pt(AsEt}_3)_2\text{Cl}_4]$ and $\text{trans-[Pt(AsEt}_3)_2\text{Br}_4]^*$ with SCN^- and SeCN^- in methanol are reported. The following reaction scheme has been proposed:



The reaction rates of the redox process are first order with respect to both the platinum(IV) complex and the reagent, Y^{n-} . Representing with k_2 the second order rate constants, it was found that the $\log k_2$ for the reactions of the various substrates with different anions are linearly related to $\log k_2$ for the corresponding reactions of the complex $\text{trans-[Pt(PPr}_3)_2\text{Cl}_4]$, (termed as $r(X)$), according to the linear free energy relationship:

$$\log k_2 = r(X) + r_s$$

(where the constant r_s depends upon the nature of the substrate). This relationship is discussed in terms of a reaction mechanism involving a weak bond formation between the platinum(IV) complex and Y^{n-} in the activated complex, probably a two electron bridged-transfer of the type:



Introduction

In previous papers we discussed some redox reactions in which platinum(IV) complexes containing π -ligands of low electronegativity are reduced to platinum(II) complexes by anions.^{1,2} A comparison of the rates of the redox reactions between the complexes *cis*- and *trans*- $[\text{Pt(PPr}_3)_2\text{Cl}_4]$ and NaSCN , NaI , KSeCN and $\text{Na}_2\text{S}_2\text{O}_3$, as reducing reagents, showed that the second order rate constants, k_2 , for the reactions of the two

substrates can be correlated by the relationship:

$$\log k_{2(\text{cis})} = \log k_{2(\text{trans})} + \text{const.} \quad (1)$$

In view of the informations that relationship of type (1) can imply, it was decided to carry out further kinetic investigation to see whether such a linear free energy relationship would be valid for a more extensive set of substrates of the type $[\text{PtL}_2\text{X}_4]$.

We report here the kinetic studies of redox reactions of *trans*- $[\text{Pt(PEt}_3)_2\text{Br}_4]$ and *trans*- $[\text{Pt(PPr}_3)_2\text{Br}_4]$ with the above reducing salts, and the redox reactions of *trans*- $[\text{Pt(PEt}_3)_2\text{Cl}_4]$, *trans*- $[\text{Pt(AsEt}_3)_2\text{Cl}_4]$ and *trans*- $[\text{Pt(AsEt}_3)_2\text{Br}_4]$ with NaSCN and KSeCN , in methanolic solutions.

Experimental Section

Materials. The complexes *trans*- $[\text{Pt(AsEt}_3)_2\text{Cl}_4]$,³ *trans*- $[\text{Pt(AsEt}_3)_2\text{Br}_4]$,³ *trans*- $[\text{Pt(PPr}_3)_2\text{Cl}_4]$,⁴ *trans*- $[\text{Pt(PEt}_3)_2\text{Cl}_4]$,¹ and *trans*- $[\text{Pt(PEt}_3)_2\text{Br}_4]$,⁵ were prepared following the methods of the literature. *trans*- $[\text{Pt(PPr}_3)_2\text{Br}_4]$ was prepared by treating a chloroformic solution of *trans*- $[\text{Pt(PPr}_3)_2\text{Br}_2]$ with bromine. The solution was evaporated and the product was recrystallized from ethanol. The isomeric form was assigned from the close similarity of its U.V. spectrum and that of *trans*- $[\text{Pt(PEt}_3)_2\text{Br}_4]$.⁶

Methanol was distilled over $\text{Mg(OCH}_3)_2$. All other materials were reagent grade.

Kinetics. The reactions of *trans*- $[\text{Pt(PEt}_3)_2\text{Cl}_4]$ with NaSCN were carried out in black painted flasks, thermostated at the desired temperature in a water bath. Samples of the reacting mixtures were withdrawn at known times, cooled at room temperature, and then measured spectrophotometrically in the range 240-360 m μ by means of an Optica CF4R recording spectrophotometer. Rates of reactions of *trans*- $[\text{Pt(PEt}_3)_2\text{Br}_4]$ and *trans*- $[\text{Pt(PPr}_3)_2\text{Br}_4]$ with $\text{Na}_2\text{S}_2\text{O}_3$ were determined spectrophotometrically by means of a stopped-flow apparatus, which consisted of a Beckman DU spectrophotometer to which was attached a rapid mixing device.

(* PEt_3 = triethylphosphine; PPr_3 = tri-n-propylphosphine; AsEt_3 = triethylarsine.

(1) A. Peloso and G. Dolcetti, *Journ. Chem. Soc.*, Submitted for publication.

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The change in transmittance with time at 360 m μ was displayed on a storage oscilloscope. All other reactions were carried out by mixing the appropriate volumes of thermostated solutions of the reactants directly in 1 cm quartz cells in the thermostat-controlled cell compartment of the spectrophotometer. At suitable time intervals the spectrum of the reacting mixture was scanned over the range 240-360 m μ . In the case of relatively fast reactions, the absorbance at a selected wavelength in the U.V. region was recorded against time. All the reactions were studied at two temperatures. For each temperature at least four different reagent concentrations were studied.

The pseudo first-order rate constants were determined from the slope of the plots of $\log(D_{\infty}-D_t)$ against time, where D_t and D_{∞} are the optical densities of the reacting mixtures at time t and after at least five half-lives, respectively.

Results

The reactions were performed using an excess of reagent, Y^{n-} , with respect to the complex in order to provide pseudo first-order conditions (the concentration of the substrate was in the range $1 \times 10^{-5} \div 1 \times 10^{-4} M$). A pseudo first-order rate law was obeyed, the reproducibility of the data being better than 5%. By plotting pseudo first-order rate constants against reagent concentrations, $[Y^{n-}]$, straight lines passing through the origin were obtained, according to the general equation:

$$-d[\text{complex}]/dt = k_2[\text{complex}][Y^{n-}] \quad (2)$$

The values of the second order rate constants, k_2 , obtained at different temperatures are listed in Table I together with the activation parameters. The error in ΔH^* is ± 1 kcal/mole and in ΔS^* is ± 3 e.u.

(a) Reactions of $\text{trans-[Pt(PEt}_3)_2\text{Cl}_4]$, $\text{trans-[Pt(PEt}_3)_2\text{Br}_4]$ and $\text{trans-[Pt(PPr}_3)_2\text{Br}_4]$ with NaSCN in methanol. The analysis of the spectral changes of the reacting mixtures showed that the platinum(IV) complexes are quantitatively reduced to $\text{trans-[PtL}_2(\text{SCN})_2]$. This product, however, undergoes a successive slower reaction, probably a polymerization process.⁷

No reproducible data were obtained in the case of the analogous triethylarsine complexes.

(b) Reactions of $\text{trans-[Pt(PEt}_3)_2\text{Br}_4]$ and $\text{trans-[Pt(PPr}_3)_2\text{Br}_4]$ with NaI in methanol. The spectral analysis of the reacting mixtures, showed that I_3^- is formed during the reaction in equimolar amount with respect to the amount of platinum(IV) reduced. From the reacting mixtures, after the reactions went to completion, $\text{trans-[Pt(PEt}_3)_2\text{I}_2]$ or $\text{trans-[Pt(PPr}_3)_2\text{I}_2]$ were precipitated by addition of water.

Few runs carried out by using methanol containing 4.3% of water gave identical kinetic results, showing that this amount of water does not affect the reaction rates.

(c) Reactions of $\text{trans-[Pt(PEt}_3)_2\text{Br}_4]$ and $\text{trans-[Pt(PPr}_3)_2\text{Br}_4]$ with $\text{Na}_2\text{S}_2\text{O}_3$ in methanol containing 4.3% of water. Water (4.3%) was added to dissolve the sodium salt.

The spectrophotometric measurements were carried out with the stopped-flow method, since the reaction rates were relatively high. The analysis of the final spectra of the solutions indicates that $\text{trans-[Pt(PEt}_3)_2\text{Br}_2]$ and $\text{trans-[Pt(PPr}_3)_2\text{Br}_2]$, respectively, are the reaction products. These complexes then undergo a successive slower substitution reaction, yielding the ionic complex $\text{trans-[PtL}_2(\text{S}_2\text{O}_3)_2]^{2-}$.

The stoichiometry of these reactions was determined by carrying out some experiments with an excess of platinum(IV) complex with respect to the thiosulfate present. From the amount of platinum(IV) complex

Table I. Specific rate constants, k_2 , and activation parameters for the redox reactions: $\text{PtL}_2\text{X}_4 + \text{Y}^{n-} \rightarrow \text{products}$

Complex	Reactant	Concn. range of reactant (moles l ⁻¹)	t, °C	k_2 (l.moles ⁻¹ sec ⁻¹)	ΔH^* (kcal/mole)	ΔS^* e.u.	
<i>trans</i> -[Pt(AsEt ₃) ₂ Cl ₄]	KSeCN	$8.4 \times 10^{-2} - 1.93 \times 10^{-2}$	50	18.8×10^{-3}	14.5	— 22	
			35	5.95×10^{-3}			
<i>trans</i> -[Pt(AsEt ₃) ₂ Br ₄]	KSeCN	$2.4 \times 10^{-3} - 4.5 \times 10^{-4}$	40	26	10	— 20	
			25	11.0			
<i>trans</i> -[Pt(PEt ₃) ₂ Cl ₄]	NaSCN	0.158 - 0.042	50	2.6×10^{-5}	17.3	— 26	
			35	0.67×10^{-5}			
	KSeCN	$8.6 \times 10^{-2} - 1.43 \times 10^{-2}$	50	9.1×10^{-2}	14.0	— 20	
			35	3.0×10^{-2}			
<i>trans</i> -[Pt(PEt ₃) ₂ Br ₄]	NaSCN	0.214 - 0.035	40	8.82×10^{-2}	15.0	— 15	
			25	2.5×10^{-2}			
	NaI	$3.2 \times 10^{-3} - 5.4 \times 10^{-4}$	40	60.2	10.6	— 17	
			25	24.3			
	KSeCN	$4.3 \times 10^{-4} - 1.43 \times 10^{-4}$	40	3.78×10^2	9.0	— 18	
			25	1.74×10^2			
	<i>trans</i> -[Pt(PPr ₃) ₂ Br ₄]	Na ₂ S ₂ O ₃	$1.5 \times 10^{-3} - 6 \times 10^{-4}$	30	1.60×10^4	10	— 7
				20	0.87×10^4		
NaSCN		0.214 - 0.027	40	4.95×10^{-2}	13.4	— 21	
			25	1.59×10^{-2}			
NaI		$2.9 \times 10^{-3} - 3.5 \times 10^{-4}$	40	38.5	9.9	— 20	
			25	16.5			
KSeCN	$4.3 \times 10^{-4} - 1.07 \times 10^{-4}$	40	2.60×10^2	7.1	— 25		
		25	1.40×10^2				
Na ₂ S ₂ O ₃	$3.7 \times 10^{-3} - 9.4 \times 10^{-4}$	40	1.55×10^4	7.6	— 15		
		25	0.8×10^4				

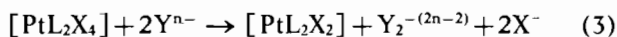
(7) R. C. Johnson and F. Basolo, *J. Inorg. Nucl. Chem.*, 13, 36 (1960).

consumed at the end of the reaction it was deduced that two thiosulphate ions per platinum(IV) are required in the redox process.

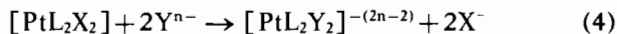
(d) *Reactions of trans-[Pt(PEt₃)₂Cl₄], trans-[Pt(PEt₃)₂Br₄], trans-[Pt(PPr₃)₂Br₄], trans-[Pt(AsEt₃)₂Cl₄] and trans-[Pt(AsEt₃)₂Br₄] with KSeCN in methanol.* In these systems at least two consecutive reactions of comparable rate were observed, so that it has been not possible to identify the product of the first reaction, which involve the disappearance of the initial platinum(IV) complex. However, by selecting appropriate wavelength, where the spectral changes are attributable to the first stage only, it was possible to calculate its rate.

Discussion

The analysis of the reaction products shows that all of the examined octahedral platinum(IV) complexes are reduced by NaSCN, NaI and Na₂S₂O₃ to square platinum(II) complexes. Whenever the stoichiometry of the reaction was determined, it was found that two molecules of reacting anion are consumed for each molecule of complex that is reduced. This suggests the common scheme for the redox reactions investigated expressed by equation (3):



Reaction (3) is followed by a nucleophilic displacement reaction on the platinum(II) complexes:



Reaction (4) could be followed only in the case of the reaction with Na₂S₂O₃. In the other cases the substitution process (4) is much faster than the redox process (3), so that [PtL₂Y₂]⁻⁽²ⁿ⁻²⁾ is the only reaction product containing platinum(II) which can be detected.

The fact that all of the reaction rates are first order with respect to the reagent, Yⁿ⁻, implies that only one of the anion molecules required by the redox process (3) is involved in the rate-determining step, the second one reacting in a successive fast step.

In Figure 1 the values of log k₂ for the examined complexes are plotted versus log k₂ (termed as r(X)) for the corresponding reactions of the complex trans-[Pt(PPr₃)₂Cl₄], selected as a standard substrate.²

It can be observed that the values obtained for each complex fall on parallel straight lines. It is also apparent that the values of log k₂ for the reactions with KSeCN do fit the appropriate lines in all the cases, suggesting that also with selenocyanate ions the same mechanism is involved.

The straight-line plots of Figure 1 obey the following linear free energy relationship:

$$\log k_2 = r(X) + r_s \quad (5)$$

where r_s depends upon the nature of the substrate. It is worth noting that equation (5) holds for both *cis* and *trans* substrates (see equation (1)).

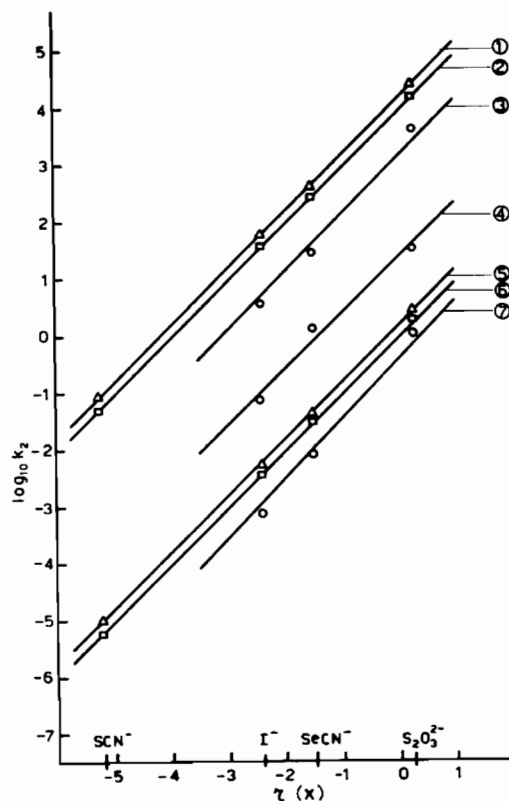


Figure 1. Correlation of the rates of reaction of Pt(IV) complexes in methanol at 40°C with the standard *trans*-[Pt(PPr₃)₂Cl₄] for different reducing anions. (1), *trans*-[Pt(PEt₃)₂Br₄]; (2), *trans*-[Pt(PPr₃)₂Br₄]; (3), *trans*-[Pt(AsEt₃)₂Br₄]; (4), *cis*-[Pt(PPr₃)₂Cl₄]; (5), *trans*-[Pt(PEt₃)₂Cl₄]; (6), *trans*-[Pt(PPr₃)₂Cl₄]; (7), *trans*-[Pt(AsEt₃)₂Cl₄]. Data for (4) and (6) taken from reference No. 2; rate data of I⁻ and S₂O₃²⁻ for reactions with (3), (5) and (7) taken from reference No. 1.

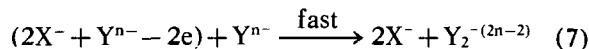
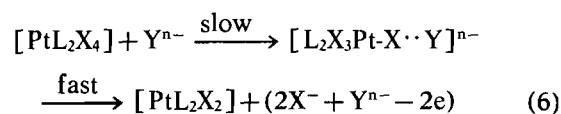
Bearing in mind that log k₂ deals with the free energy of activation, relationship (5) suggests that each reducing agent makes a contribution to the free energy of activation of the redox process (3) independent of the nature of the substrate. In other words, bond-making and bond-breaking are kinetically independent in these processes. This can be explained on the basis of a weak bond formation in the activated complex. In fact, if a marked extent of bond formation is developed in the transition state, one should expect that the degree of interaction between the complex and the reducing agent be strongly dependent upon the nature of the substrate. Therefore the substrates studied should exhibit a different discrimination ability toward the reacting anions, owing to their different geometrical and chemical nature. As a consequence, the occurrence of a bimolecular nucleophilic substitution at platinum(IV) in the rate determining step seems to be very unlikely. It is pertinent to note that S_N2 processes at platinum(IV) centers have never been observed.⁵

The formation of an activated complex involving a small (or no) extent of bond formation is in agreement with an inner- or an outer-sphere electron transfer mechanism. In these cases the role played by the nature of the substrate in determining the activation energy of the redox reaction is related to two main

factors: (i) the overall deformability of the solvated substrate, *i.e.* the energy required to make it available for the electron transfer (this factor depends upon the nature of all the coordinated ligands and their stereochemical arrangement); (ii) the presence in the substrate of ligands able to act as preferential reaction centers, *i.e.* to act as electron mediators.⁸

Although a choice between the outer- and inner-sphere mechanism is not possible on the basis of the present data, some indications on the mechanism can be inferred from the well known ability of platinum(IV) complexes to undergo «substitution» reactions through catalytic processes involving redox reactions with bridged atom transfer.^{9,10} Thus, we suggest that the redox reaction (3) proceeds through a two-electron transfer mechanism involving a bridged activated complex with a weak bond formation between the reagent

and one of the halogens of the substrate:¹¹



According to this mechanism, the bromo-complexes react faster than the corresponding chloro-complexes owing to the better ability of bromide with respect to chlorine to act as electron mediator.⁸

Activation parameters in Table I show that the change in the reaction rates for different substrates reacting with the same anion are mainly due to the changes in the enthalpy of activation, the entropy term being nearly constant.

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(10) A. Peloso and G. Dolcetti, *Gazz. Chim. Ital.*, 97, 120 (1967) and references therein.

(11) G. Dolcetti, A. Peloso and M. L. Tobe, *Journ. Chem. Soc.*, 5196 (1965).