

Kinetics and Mechanisms of Substitution Reactions with Sulphur-containing Nucleophiles in Aqueous Acid Solutions. II^a. Rates of Reactions of Some Tetrahalopalladate(II) Anions with Some N-Alkyl Substituted Thioureas

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The rates and activation energy parameters of halide ligand substitution in PdX_4^{2-} ($X = Cl^-, Br^-$), with N-alkyl substituted thioureas in aqueous halo acid solutions have been determined for the first kinetically distinguishable step. Ligand and product composition is substantiated by analytical data. Low enthalpies and an appreciably negative entropy of activation accompany high rates of reaction.

The rate law in each case is $k_{obs} = k [L]$, where $L =$ N-alkylsubstituted thioureas and k , the ligand dependent rate constant at 25 °C.

Introduction

Many studies on the kinetics and mechanisms of ligand substitution in metal ion complexes possessing various geometries have been reported [1–3]. A general and consistent pattern of behaviour seems to have emerged for ligand substitution in four coordinated square-planar complexes of d^8 metals. This pattern is characterized by the two-term rate law, viz., $k_{obs} = k_1 + k_2 [Y]$ [4], in which the rate constant, k_1 , independent of the concentration of the incoming nucleophile, is attributed to the rate-determining generation of the solvo species. Several studies have been published in which this term is not observed, indicating that the solvospecies is either not generated [5, 6] or, if generated, is ineffective with respect to the reaction with the incoming nucleophile and hence generation of the product [7]. Whether or not the ligand-independent path appears in the rate law for a particular reaction depends on the relative magnitudes of the rates of the two consecutive reactions.

By systematic variation of the reactants a deviation from the general pattern of behaviour could be accomplished [8]. An exploitation of the factors which cause this deviation could lead to a fuller understanding of the substitution process [9]. Parameters

which have a marked effect on the kinetics and mechanisms of substitution in square-planar complexes are:

(i) bulky ligands, attached to the metal ion, which tend to block the axial positions and thereby hinder the associative mechanism [9, 10];

(ii) the ionic strength of the reaction medium [11–14], which considerably influences cationic, anionic and neutral substrates;

(iii) the positions occupied by two identical ligands in the metal ion, generates either a *cis*- or *trans*-species the reactivity of which differs considerably [2].

The extensive information on the Pt(II)-system rendered the arrangement of the most common nucleophiles in a series according to the n_{Pt}° scale possible [2]. On the n_{Pt}° scale the reactivity of a nucleophile, towards a common substrate, *trans*-[Pt(py)₂Cl₂], in methanol at 30 °C is evaluated. This exercise kindled the general interest in rate processes of other square-planar complexes.

At present the effect that the solvent (in particular, mixed, aqueous and non-aqueous, solvents) has on the rate processes is receiving considerable attention [15]. In an earlier publication [23] it was stated that the ligand independent term was negligible when the halides in $PdCl_4^{2-}$ and $PdBr_4^{2-}$ are substituted with thiourea. This paper expands previous work to include the study of halide substitution in the same substrates used before with a series of N-alkyl substituted thioureas, and indicates the temperature dependence of the rate processes.

Experimental

Chemicals

Hydrobromic acid (47 per cent) and hydrochloric acid (32 per cent) were of Merck's *pro analysi* grade. Doubly distilled water obtained with a quartz still was passed through an "Algastat" cation exchanger bed, before use.

^aFor part I see [23].

TABLE I. Analytical Data for the Different N-alkyl Substituted Thioureas.

Formula	Melting Point ^a	%N		%C		%H		%S	
		calcd	found	calcd	found	calcd	found	calcd	found
CH ₃ NHCSNH ₂ (mtu)	115 °C	31.11	30.46	26.67	27.26	6.67	6.70	35.56	37.18
C ₂ H ₅ NHCSNH ₂ (ettu)	105 °C	26.92	26.22	34.61	35.87	7.69	7.89	30.77	31.63
CH ₃ NHCSNHCH ₃ (dimtu)	45 °C	26.92	26.29	34.62	35.51	7.69	7.61	30.77	31.86
C ₂ H ₅ NHCSNHC ₂ H ₅ (diettu)	56 °C	21.21	25.45	45.45	46.74	9.09	10.47	24.24	20.17

^aMelting points corrected.

TABLE II. Analytical Data for the Pd(II) Complexes.

Formula	Melting point ^a	%N		%C		%H		%S		%Cl	
		calcd	found	calcd	found	calcd	found	calcd	found	calcd	found
Pd(mtu) ₄ Cl ₂	198 °C	20.84	20.8	17.86	18.05	4.46	4.39	23.82	24.17	13.19	13.18
Pd(ettu) ₄ Cl ₂	203 °C	18.87	18.23	24.27	24.01	5.39	5.49	21.57	19.33	11.95	13.70
Pd(diettu) ₄ Cl ₂	177 °C	15.88	12.95	34.03	44.99	6.80	8.31	18.15	14.21	10.05	8.49
Pd(dimtu) ₄ Cl ₂	360 °C	18.87	19.31	24.27	24.68	5.39	5.34	21.57	21.50	11.95	12.07

^aMelting points corrected.

The N-alkyl substituted thioureas studied, *viz.*, N,N'-dimethylthiourea (*dimtu*); N-methylthiourea (*mtu*); N-ethylthiourea (*ettu*); N,N'-diethylthiourea (*diettu*) were obtained from K & K Laboratories, Hollywood, California. Following recrystallization from methanol and vacuum desiccation for six hours each salt was subjected to microanalysis.

Palladium(II) complexes were prepared following the method of Kurankov [16]. Aqueous hydrochloric acid solutions of K₂PdCl₄ and a series of different N-alkyl thioureas were mixed on the water bath. From the dark-red solutions, fine orange-red needle-like crystals were obtained after the addition of concentrated hydrochloric acid. The product was purified by recrystallization from warm water. The crystals were dried for six hours under vacuum after washing with methanol, and then subjected to microanalysis.

The analyses of the different complexes are collected in Tables I and II. The spectra of the complexes obtained were recorded with a Cary 15 recording spectrophotometer using matched quartz cells.

Results and Discussion

Kinetics

All kinetic runs were obtained with a custom-built stopped flow apparatus, previously described [17]. To ensure pseudo first-order kinetics the concentration of the entering ligand was in sufficient excess relative to that of the substrate. In addition

the ionic strength of the reaction mixtures was kept constant at 2.0 M, to curb the influence of the salt effect on the rate processes [18]. To prevent deprotonation of the aquotrihalopalladate(II) anion, all solutions, including that of the incoming nucleophile were made up in 2.0 M aqueous hydrochloric/hydrobromic acid. In each run equal volumes of substrate and nucleophile were mixed in the stopped-flow apparatus, while the transient absorbance of each reaction mixture was recorded by a Tektronix, Model 5031, storage oscilloscope. Plots of the change in absorbance with time were obtained in the usual way and were curved, indicating that two consecutive reactions were occurring, *viz.*, a rapid reaction followed by a much slower one [19]. The half-lives of these consecutive reactions which differed approximately by a factor of ten, were determined by a curve-stripping technique [20]. From this data the pseudo first-order rate constants of the first distinguishable step were calculated and are listed in Table III. From a temperature dependence study the activation parameters, ΔH^\ddagger , ΔS^\ddagger were determined and are presented in Table IV.

Taking cognizance of previously reported studies [21], the first rate-determining step coincides with the first kinetically distinguishable step and is the replacement of the first halide ligand by the entering nucleophile, while the replacement of the third halide ligand represents the second distinguishable step, the rate constant being $k_3 \approx 10 \times k_5$. Because the substituted thioureas have high *trans* activation, the rate of replacement of the second and fourth halide ligands is fast and not kinetically observed and the

TABLE III. Rate Data.

a) Kinetic Data for the Reaction $\text{PdCl}_4^{2-} + \text{X} \rightarrow$ in 2.0 M Aqueous HCl; $\mu = 2.1 M$.				b) Kinetic Data for the Reaction $\text{PdBr}_4^{2-} + \text{X} \rightarrow$ in 2.0 M Aqueous HBr; $\mu = 2.1 M$.									
	k_{obs} , sec^{-1}	No. of runs	Slope, $M^{-1} \text{sec}^{-1}$	t , $^{\circ}\text{C}$		k_{obs} , sec^{-1}	No. of runs	Slope, $M^{-1} \text{sec}^{-1}$	t , $^{\circ}\text{C}$				
$\text{X} = [\text{mtu}] \times 10^3$				$\text{X} = [\text{mtu}] \times 10^4$									
20	118	7	$6.0 \pm 0.1 \times 10^3$	4.3	40	70.5	5	$2 \pm 0.1 \times 10^4$	25				
10	60.7	5			20	35.8	5						
5	31.5	5			10	19.1	5						
—	—	—			5	8.7	5						
8	50	4			—	—	—						
4	24.7	6	$6.25 \pm 0.1 \times 10^3$	4.5	—	—	—	$1.25 \pm 0.1 \times 10^4$ *	12.5				
2	12.0	3			160	144	5						
—	—	—			80	70	5						
5	76	15			40	34.5	5						
2.5	38	12			—	—	—						
1.25	19.7	6	$1.5 \pm 0.1 \times 10^4$	13.7	$\text{X} = [\text{dimtu}] \times 10^4$								
—	—	—			80	86	5	$1.63 \pm 0.1 \times 10^4$	11.1				
$\text{X} = [\text{dimtu}] \times 10^3$					40	66.0	5						
16	42.2	7			20	31.0	5						
8	19.7	5			10	16.3	5						
4	10	3	—	—	—								
—	—	—	$2.65 \pm 0.1 \times 10^3$	4.3	80	115	5	$1.8 \pm 0.1 \times 10^4$	12.5				
8	30.3	4			40	76	5						
4	15.4	5			20	36.5	3						
2	8.0	7			10	16.0	4						
—	—	—			—	—	—						
8	51.5	3	$3.8 \pm 0.1 \times 10^3$	12.5	160	156	5	$9.8 \pm 0.1 \times 10^3$	4.3				
4	26.5	2			80	87.5	6						
2	12.35	5			40	40	4						
—	—	—			—	—	—						
$\text{X} = [\text{ettu}] \times 10^3$					$\text{X} = [\text{ettu}] \times 10^4$								
20	92.5	7	$4.6 \pm 0.1 \times 10^3$	4.3	160	136	5	$8.5 \pm 0.1 \times 10^3$	4.3				
10	47.6	6			80	71.5	5						
5	23.5	5			40	34.7	4						
—	—	—			—	—	—						
8	40.5	5			20	38.7	7						
4	21.0	4	$5.06 \pm 0.1 \times 10^3$	12.5	10	19.3	3	$1.9 \pm 0.1 \times 10^4$	12.5				
2	10.5	5			5	10.8	2						
—	—	—			—	—	—						
8	85	25			80	102	5						
4	41.6	15			40	61	5						
2	21	9	$1.0 \pm 0.1 \times 10^4$	25.1	20	38.8	5	$1.8 \pm 0.1 \times 10^4$	12.0				
1	10.25	5			10	17.5	5						
—	—	—			—	—	—						
$\text{X} = [\text{diettu}] \times 10^3$					$\text{X} = [\text{diettu}] \times 10^4$								
10	37	7			$3.7 \pm 0.1 \times 10^3$	4.3	40			65	5	$1.74 \pm 0.1 \times 10^4$	12.5
5	17.8	5	20	34.8			5						
2.5	6.7	3	10	17.35			3						
—	—	—	—	—			—						
16	59.2	5	160	141			7						
8	29.4	6	$4.8 \pm 0.1 \times 10^3$	12.5	80	68.7	7	$8.8 \pm 0.1 \times 10^3$	4.3				
4	15.7	4			40	32.5	4						
—	—	—			—	—	—						
8	60.8	7			—	—	—						
5.5	40.3	7			$7.45 \pm 0.1 \times 10^3$	25	2			16.7	6		
2	16.7	6	—	—			—						

*Calculated from $\log k$ vs. $1/T$ plots.

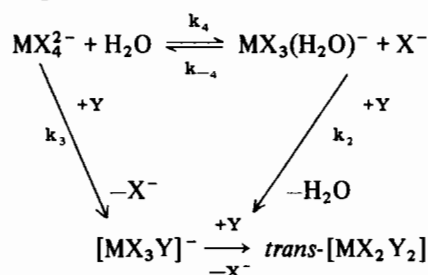
TABLE IV. Activation Parameters.

[X]	ΔF^\ddagger , kcal	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , e.u./mol
(a) $\text{PdCl}_4^{2-} + \text{X} \rightarrow$ in 2.0 M aqueous HCl; $\mu = 2.1 \text{ M}$ 25 °C			
tu [23]	11.2	5.0	-19.5
mtu	11.7	7.2	-15
ettu	11.2	6.1	-17
dimtu	12.1	6.7	-18
diettu	12.2	5.0	-24
seu [23]	11.2	2.0	-31
(seu = selenourea)			
(b) $\text{PdBr}_4^{2-} + \text{X} \rightarrow$ in 2.0 M aqueous HBr; $\mu = 2.1 \text{ M}$			
tu [23]	11.6	6.6	-16.8
mtu	11.6	5.8	-19.5
ettu	11.7	5.4	-21.0
dimtu	11.7	3.5	-27.5
diettu	11.0	13.0	+6.7
seu [23]	10.2	11.4	+4.0

rates of replacement of the first and third halide ligands become rate-determining [22].

The mechanism

It has been suggested previously [23] that the mechanism which is operative in similar square-planar systems could be accounted for in the following scheme:



(where M = Pd(II); X = Br⁻, Cl⁻ and Y = an N-alkyl substituted thiourea nucleophile).

The unabridged rate law derived for this proposed scheme incorporates a steady-state condition for $\text{MX}_3(\text{H}_2\text{O})^-$, and is:

$$k_{\text{obs}} = k_3 + \left[\frac{k_4 k_2}{k_2 [\text{Y}] + k_{-4} [\text{X}]} \right] [\text{Y}]$$

This expression may be simplified considerably when certain limiting conditions are imposed, viz.,

(i) $k_2 [\text{Y}] \gg k_{-4} [\text{X}]$, the familiar two-term rate law, $k_{\text{obs}} = k_3 [\text{Y}] + k_4$ being derived.

(ii) $k_2 [\text{Y}] \approx k_{-4} [\text{X}]$. Since the kinetics of the reactions reported in this paper were studied using 2.0 M aqueous halo acid solutions, the limiting conditions in (i) did not apply. In order to obtain the

value of k_{obs} it was necessary to determine the relative value of each term. Although the aquo-halo species of $[\text{PdCl}_3(\text{H}_2\text{O})]^-$ is up to ten times [24] more reactive than $[\text{PdCl}_4]^{2-}$, the rates of the reactions with the $[\text{PdCl}_2(\text{H}_2\text{O})]^-$ substrate had no influence even when the ratio of $[\text{PdCl}_4]^{2-} : [\text{PdCl}_3(\text{H}_2\text{O})]^-$ varied between 40:1 and 2:1 when $2.0 \text{ M} > [\text{Cl}^-] > 0.1 \text{ M}$ [25]. The higher reactivity of $[\text{PdCl}_3(\text{H}_2\text{O})]^-$ relative to $[\text{PdCl}_4]^{2-}$ was invariably based on the rates of reaction with hard nucleophiles, namely amines [26, 27], N-alkyl substituted amines [26, 27] and 1,10-phenanthroline [24] which form Pd-N bonds with these nucleophiles. Because the softness of the nucleophiles increases in the order $\text{H}_2\text{O} < \text{Cl}^- < \text{Br}^-$, the softness of the substrates increases too as follows: $[\text{PdCl}_3(\text{H}_2\text{O})]^- < [\text{PdCl}_4]^{2-}$. Thus the N-alkyl substituted thioureas are biphilic reagents which possess anomalously high reactivity, as the nucleophilic reactivity constants of sulphur-containing nucleophiles on the n_{Pt}° scale indicate. Thiourea manifests its high reactivity toward many metal ions only under certain conditions. It was observed [39] that some reactions occur only in nonaqueous solvents, while others occur in aqueous solutions only with metal ions which are not hydrolyzed or which are weakly hydrolyzed. The N-alkyl substituted thioureas appear to be much more reactive toward the soft $[\text{PdBr}_4]^{2-}$ and $[\text{PbCl}_4]^{2-}$ than toward the aquotrihalopalladate(II) species, and it is suggested that the values of k_2 and k_3 are comparable. In addition, the specific rate constants [28, 29] $k_4 = 8.9 \text{ sec}^{-1}$ and $k_{-4} = 180 \text{ M sec}^{-1}$. In the most unfavourable cases the ratio $[k_2 k_4 / (k_2 [\text{Y}] + k_{-4} [\text{X}])] / k_3$ is calculated to be less than 2 percent.

The general rate law reduces to $k_{\text{obs}} = k_3 [\text{Y}]$. Plots of k_{obs} vs. $[\text{Y}]$ are linear and pass through the origin, the slopes represent the second-order rate constants which are ligand-dependent as the rate law requires.

It is known that alkyl substitution in an atom of nucleophile neighbouring the ligating atom is governed by an inductive effect. A series of entering nucleophiles, in which the bulkiness was systematically increased, was formed by progressive N-alkyl substitution in the thiourea molecule.

The Rate Constants

A comparison of the ligand dependent rate constants, k_3 , for displacing the first halide ligand in PdCl_4^{2-} and PdBr_4^{2-} respectively for the nucleophiles tu, mtu, ettu, dimtu, diettu is 4.3×10^3 [23]; 6.0×10^3 ; 4.6×10^3 ; 2.6×10^3 ; 3.7×10^3 and 8.0×10^3 [23]; 8.75×10^3 ; 8.5×10^3 ; 9.75×10^3 ; 8.8×10^3 for the chloro and bromo systems, respectively. In the chloro system the rate of substitution with the series of mono substituted thioureas increases slightly, while the doubly substituted thioureas show a decrease in the rate constants. In the bromo system the rate

constants increase with increased bulkiness of the thiourea molecule. The higher reactivity of the bromo system could be ascribed to PdBr_4^{2-} being a softer substrate than PdCl_4^{2-} towards the soft incoming thioureas.

The Effect of Structure

The coplanarity of C, N and S in the thiourea molecule, established by crystal structure study [30], is unchanged by complex formation. The sp^2 hybridized orbitals of sulphur are used in metal-sulphur bonding, while the π -orbitals are normal to the molecular plane. In the $\text{Pd}(\text{tu})_4^{2+}$ unit, the four tu groups are not completely coplanar but are tipped relative to the approximately square " PdS_4 "-plane by 43° – 60° and twisted relative to the " Pd-S-C -line" by 17° – 26° [25]. It is tempting to explain these orientations in terms of hydrogen bonding and packing considerations. These tilts and twists are necessitated in order to utilize the empty non-bonding 3d orbitals on the S atom because it is not energetically favourable to remove an electron from the metal d_{π} -orbitals to the thiourea " a_1 " antibonding MO.

Deductive reasoning, substantiated by an infrared study reported by Yamaguchi *et al.* [32], suggests that the thiourea molecule bonds to the metal ions Pd(II) and Pt(II) through the sulphur atom. The dipole moment of thiourea [33] has been interpreted as indicating a resonance hybrid with 20 to 30 per cent contribution of highly polar structures. In a recently published report, Figuera and Menéndez [34] calculated that the negative charge on the S-atom of the thiourea molecule remains unchanged when N-alkyl substitution is accomplished. This observation fits the kinetic data within the limits of experimental error.

The Solvent Route

In this particular study the solvent route appeared to be completely absent or ineffective in the generation of the product. A substantial number of studies have reported similar observations. Mureinik [35] recently reported on the replacement of the halide ligands in PtCl_4^{2-} with thiocyanate and reported $\text{PtCl}_3(\text{H}_2\text{O})$ to be inactive towards the thiocyanate nucleophile, even under the most favourable conditions. The concentration of $[\text{PtCl}_3(\text{H}_2\text{O})]^-$ was increased to 26% of the initial concentration of the complex by the addition of an equimolar amount of silver nitrate solution to the initial substrate solution.

Cusumano *et al.* [36], reported that the rates of substitution of X in axially blocked $[\text{Pd}(\text{Et}_4\text{dien})\text{X}]^+$ where X = Cl, Br or I is controlled by the solvolytic path (in methanol) only, since steric hindrance of the N-alkyl substituted amines prevents the ligand from associating with the precursor. Roulet and Gray [9] reported on the reaction of halide ions with $[\text{Pd}(\text{Et}_4\text{-dien})\text{X}]^+$, ($\text{Et}_4\text{dien} = \text{HN}[\text{C}_2\text{H}_4\text{N}(\text{C}_2\text{H}_5)_2]_2$; X = Cl^- ,

Br^- , I^-) complexes. The activation in protic solvents is associative whereas in aprotic solvents a dissociative mechanism is probable. This was re-examined by Palmer and Kelm [37] who used higher nucleophile concentrations than those previously reported by Roulet and Gray and found in the majority of these cases that the traditional two term rate law applied.

The solvolytic path accounts entirely for the exchange reaction of $^*\text{Cl}^-$ with PtCl_4^{2-} [38].

A very extensive study of thiourea complexes was made by Golovnia and Prokofeva [39] and concluded that only those metal ions which do not hydrolyze, or in which hydrolysis is suppressed react with thiourea. It would appear that the exact conditions under which the solvated metal ions would not react with an incoming nucleophile have yet to be determined [7]. The mechanisms of ligand substitution and solvent exchange are similar [40], while a comparison of some of these reactions with metal cations [41] has shown these processes to be related by structural properties of the solvent medium.

Entropy-enthalpy relations may provide another link between reaction rates and structural factors [42]. The rate of ligand substitution in octahedral complexes in water is largely determined by the rate of dissociation of a solvent molecule from the inner coordination sphere [40]. The structural properties of the solvent, *viz.*, "stiffness" and "openness" are mainly responsible for differences in ΔH^\ddagger and ΔS^\ddagger . This common origin explains why ΔH^\ddagger and ΔS^\ddagger are correlated in an *iso*-kinetic plot [40], which forms a good example of the so-called "Compensation law", *i.e.*, the linear enthalpy-entropy effect. This effect has recently been discussed in depth by Leffler [43] and Brown [44]. Furthermore the linearity observed is the basis of the "linear free energy relationship" which came into prominence with the Hammett equation [45].

From a limited number of activation parameters relating to substitution reactions in square-planar complexes, it would appear that each entering nucleophile of any series, having similar steric properties, as in the series utilized in this study, is related by an *iso*-kinetic plot. Similar intercept would indicate a similar value for ΔH^\ddagger . Plots of ΔH^\ddagger vs. ΔS^\ddagger for the substitution of the halide ligands in PdBr_4^{2-} and PdCl_4^{2-} , with N-alkyl substituted thioureas in aqueous hydrobromic/hydrochloric acid solution respectively appear in Fig. 1. The intercept, $\Delta H^\ddagger = 11.2 \text{ kcal mol}^{-1}$, compares very favourably with the enthalpy of solvation of PdBr_4^{2-} , $\Delta H^\ddagger = 11 \pm 1 \text{ kcal mol}^{-1}$, reported by Elding [46]. Higher reaction rates in this study parallel lower enthalpy values, which is in agreement with the data of Chang and Wong [47] for the following study, *viz.*, $\text{Pt}(\text{dien})\text{Br}^+ + \text{X-py} \rightarrow \text{Pt}(\text{dien})(\text{X-py})^{2+}$ (where dien = diethylenetriamine, X-py = a derivative of pyridine). The enthalpy value of $\Delta H^\ddagger = 19.5 \text{ kcal mol}^{-1}$, which has been obtained

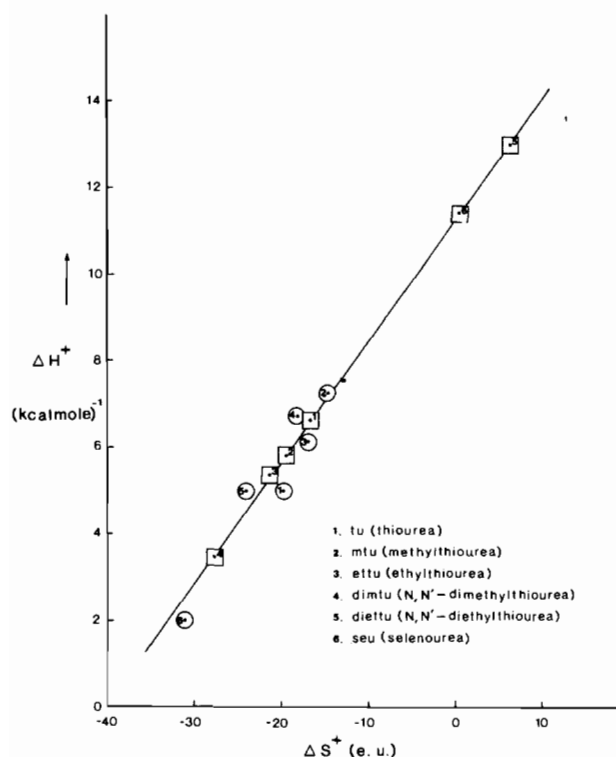
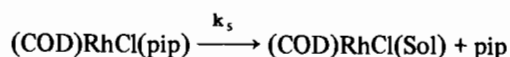


Fig. 1. Isokinetic plot for the reactions: $\text{PdCl}_4^{2-} + \text{X}$ (○); $\text{PdCl}_3\text{X}^- + \text{Cl}^-$ (○); $\text{PdBr}_4^{2-} + \text{X}$ (□); $\text{PdBr}_3\text{X}^- + \text{Br}^-$ (□).

in the solvent step agrees remarkably with the $\Delta H^\ddagger = 21.1 \text{ kcal mol}^{-1}$, obtained from the intercept of ΔH^\ddagger vs. ΔS^\ddagger plot. Nicholson [48] reported on the reactions of $\text{CODRhCl}(\text{pip})$ with a series of ethylenediamines (where COD = cycloocta-1,5-diene and pip is piperidine). Iso-kinetic plots for various ethylenediamines, viz., en (ethylenediamine), Nen (*N*-methyl-ethylenediamine); N_2en , (*N*₂-dimethylethylenediamine) (*asym*); NenN' (*N,N*-dimethylethylenediamine) (*sym*); N_2enN (*N*₂,*N'*-trimethylethylenediamine); $\text{N}_2\text{enN}'_2$ (*N*₂,*N'*-tetramethylethylenediamine); were utilized in this study, and consist of three straight lines in each set, viz.,

- (i) en, Nen and N_2en
- (ii) NenN' ; $\text{N}_2\text{enN}'$ and
- (iii) $\text{N}_2\text{enN}'_2$,

indicating that these amines display different steric structures. Furthermore, the intercept of this plot, $\Delta H^\ddagger = 11.9 \text{ kcal mol}^{-1}$, compares very favourably with the enthalpy of activation for the solvolysis reaction,



for which $\Delta H^\ddagger = 11.4 \text{ kcal mol}^{-1}$.

Nicholson [48] considered the slightly higher enthalpy obtained with the less substituted ethylenediamines to indicate the degree of perturbation

caused in the solvent structure around the substrate. For both the chloro and bromo systems reported in this study, the less substituted thioureas too (with one exception) are associated with higher enthalpy and for similar reasons. The reaction of *N,N'*-diethylthiourea with PdBr_4^{2-} (referred to above) is associated with an activation enthalpy twice that for thiourea with PdBr_4^{2-} and exhibits a positive ΔS^\ddagger , $+6.7 \pm 0.3 \text{ cal deg}^{-1} \text{ mol}^{-1}$. The degree of solvation seems to be proportional to the number of methyl groups present in ethylenediamine, which would require less energy to move into the solvation sphere in order to react, because of the "solvent-like" character of ethylenediamine. After the model of Frank and Wen [49], this would cause less perturbation of the solvent structure.

The sp^2 hybridized C atom in the thiourea molecule would result in a wedge shaped structure for the *N,N'*-diethylthiourea molecule. Together with this increased steric hindrance the incoming group would experience increasing difficulty on approaching the reactive sites of the substrate. This would lead to an increase in ΔH^\ddagger , while the entropy of activation would become more positive as a result of the smaller degree of solvation in the transition state, which can be envisaged as the "setting free" of solvent molecules to attain the transition state.

The substitution [50] of the solvent molecule, methanol, in *trans*- $[\text{Pt}(\text{PEt}_3)_2(\text{mesityl})\text{MeOH}]^+$ with 2-methylpyridine is characterized by a positive ΔS^\ddagger value of $+13.4 \pm 0.6 \text{ cal deg}^{-1} \text{ mol}^{-1}$, which could be due to a sterically induced discharge of solvent molecules from the hydrocarbon-like exterior of the activated complex into the disordered region which borders the bulk solvent. All the other members of the series reported by Romeo *et al.* [50] have large negative activation entropies. The slope of their ΔH^\ddagger vs. ΔS^\ddagger plot is reported to be 350 K while for both the chloro and bromo systems a value of 285 K is obtained in this study, which reflects the more negative values of ΔS^\ddagger .

It would appear that the polarity of the reactants has a definite bearing on the activation entropies. In this particular case a neutral nucleophile reacts with a substrate, *trans*- $[\text{Pt}(\text{PEt}_3)_2(\text{mesityl})\text{MeOH}]^+$, which has a single positive charge. It was hoped that the rate of substituting the halide ligands in tetrahalopalladium(II) anions with bulky *N*-alkyl substituted thiourea would be considerably slower than that of thiourea, it proved the opposite. The wedge-like structure of the ligands varies very little, thus it does not diminish the accessibility of exposed sulphur atom to the direct association with the substrate.

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