Inorganica Chimica Acta, 63 (1982) 9–11

Kinetics of the Reaction of *trans*-Dichlorobis(pyridine)platinum(II) with Phenyl Methyl Sulfides and Sulfoxides

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Received March 31, 1982

The reactions of trans-$Ptpy_2Cl_2$ *with a series of 4-substituted phenyl methyl sulfides and sulfoxides have been studied conductimetrically at 30 °C in methanol. The substitutions of these ligands can be described by the equation:*

$$k_{obs} = \{k_1 + k_2[L]\}[Complex]$$

and both sulfides and sulfoxides exhibit linear free energy relationships with the Hammett σ constants of the substituents even though the sulfides are more reactive than the respective sulfoxides by a factor of twenty or more.

Introduction

The substitution reactions of platinum(II) have long been employed as models for square planar reactivity and the general mechanism of such reactions has been summarized in several recent articles [1–3] and a general molecular orbital description has also appeared [4]. Although many of the investigations in this area have involved neutral amines, phosphines, and sulfides in various roles relative to Pt(II) substrates (*i.e.*, as entering and leaving groups as well as in *cis* or *trans* positions relative to the leaving/entering group), this work has recently been extended to include sulfoxides (primarily dimethylsulfoxide) in many of these same roles [5]. In an effort to add to our knowledge about the reactions of square planar complexes and the reactivities of different types of sulfur-containing ligands we have studied the reaction kinetics for a series of substituted phenyl methyl sulfides and sulfoxides toward the substrate *trans*-$Ptpy_2Cl_2$.

Experimental

Materials

Sulfoxides were synthesized by using a 1:1 mole ratio of hydrogen peroxide in methanol at 0 °C to oxidize the respective sulfides [6] which were obtained commercially or prepared by reacting methyl iodide or dimethyl sulfate with the sodium salt of the appropriate thiophenol [7] as described previously [8]. *Trans*-$Ptpy_2Cl_2$ was synthesized by a standard method [9]. Methanol was purified by distillation immediately prior to use.

Kinetics

Reaction rates were determined at 30.0 ± 0.1 °C by monitoring the conductivities of solutions in Erlenmeyer conductance cells (cell constants = 0.1347 and 0.1763 cm^{-1} as determined with aqueous KCl solutions) [10]. Pseudo first-order conditions were maintained at all times by utilizing at least a 100-fold excess of sulfide or sulfoxide ($Ptpy_2Cl_2$ = 1.0×10^{-4} *M*, sulfide $\geqslant$ 0.010 *M*, sulfoxide $\geqslant$ 0.10 *M*) and rate constants (k_{obs}) were calculated by the Guggenheim method [11] from measurements made at regular intervals during two one-hour spans separated by a period of at least two hours. Rate constants were obtained for each ligand at three different ligand concentrations by averaging the values for at least three separate kinetic runs at each concentration.

Results and Discussion

The final conductances measured for the reaction mixtures of *trans*-$Ptpy_2Cl_2$ and the sulfide or sulfoxide ligands (L) correspond to the behavior expected for 1:2 electrolytes, suggesting that all of these species displace two chloride ions to form $Ptpy_2L_2^{2+}$. Despite this fact, all of these reactions follow first order kinetics, which implies that these

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0020-1693/82/0000-0000/$02.75

TABLE I. Kinetic Data for *trans*-$Ptpy_2Cl_2 + 2L \rightarrow$ *trans*-$Ptpy_2L_2^{2+} + 2Cl^-$ in Methanol at 30 °C.

$L = XC_6H_4SCH_3$	σ	$k_2 \times 10^3$ (s^{-1} m^{-1})	$-\log k_2$
$X = CH_3O$	−0.268	13.8	1.86
CH_3	−0.170	6.73	2.25
H	0	7.61	2.11
Cl	0.373	4.3	2.37
$L = XC_6H_4S(O)CH_3$			
$X = CH_3O$	−0.268	0.565	3.25
CH_3	−0.170	0.156	3.81
H	0	0.310	3.51
$L = XC_6H_4SC_6H_5$ (ref. 18)			
$X = CH_3O$	−0.268	1.70	2.27
H	0	0.64	3.19
Cl	0.373	0.69	3.16

substitution reactions occur *via* the two step process:

$$trans\text{-}Ptpy_2Cl_2 + L \rightarrow Ptpy_2LCl^+ + Cl^- \qquad (1)$$

$$Ptpy_2LCl^+ + L \rightarrow Ptpy_2L_2^{2+} + Cl^-, \qquad (2)$$

with the first step being rate limiting, and that of eqn. 2 following rapidly.

When the values for the pseudo-first order rate constants (k_{obs}) obtained from the Guggenheim analyses are plotted against the ligand concentration at constant complex concentration, the result is a series of straight lines with a non-zero intercept as shown in Fig. 1. This behavior is consistent with the two-term rate law that has been found to apply to the reactions of square-planar complexes in methanol (eqn. 3):

$$k_{obs} = \{k_1 + k_2[L]\}[Complex] \qquad (3)$$

where L represents the concentration of the incoming ligand. The common intercept gives the value of k_1, the rate constant for the solvent-assisted reaction pathway while the slopes of the lines yield values for k_2, the rate constant for the direct replacement of chloride by the incoming ligand. The value obtained for k_1 (~3×10^{-5} sec^{-1}) agrees well with the value found previously at this temperature [12]. A comparison of the k_2 values for these ligands, listed in Table I, provides a great deal of insight into their relative reactivities.

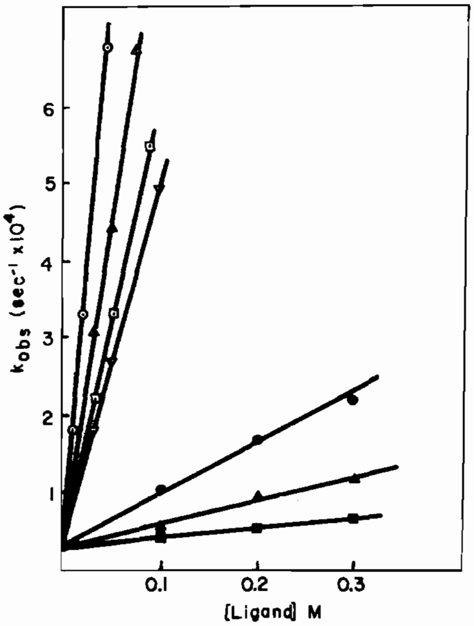

Fig. 1. Plot of k_{obs} *vs.* [L] for $L = XC_6H_4SCH_3$ (open symbols) and $XC_6H_4S(O)CH_3$ (closed symbols) $X = CH_3O$ (⊙), CH_3 (△), H (⊡), and Cl (▽).

The most notable observation is the much lower reactivities of the sulfoxides relative to the corresponding sulfides (by a factor of ~25), as has also been observed for the reaction of selected sulfides and sulfoxides toward K_2PtCl_4 [13]. The potentially ambidentate nature of the sulfoxide group introduces the possibility that these species could be interacting with Pt *via* the oxygen atom rather than the sulfur. Although the sulfur atom is the usual donor site for sulfoxides toward platinum(II) [14], and PtL_2Cl_2 compounds in which L represents the same phenylmethyl sulfoxides studied here have been isolated and found to be S-bonded (by means of infra-red measurements) [15], the report of O-bonded sulfoxides in cationic platinum compounds, especially those with severe steric requirements [16] demanded that this question be examined. Although all attempts to isolate solid products from these solutions were unsuccessful, the infra-red spectra of the residues obtained by evaporating reaction mixtures exhibit the positive ν_{SO} expected for sulfur bonding [17]. Thus, the differences in reactivity between the respective sulfides and sulfoxides must be attributed to the change in nucleophilicity of the sulfur which is induced by appending an oxygen atom rather than to a change in the donor site.

Somewhat smaller in magnitude, although no less significant, are the differences in reactivity among the various sulfides and sulfoxides as the substituents on the benzene ring are changed. Both sets of ligands exhibit a decrease in reactivity (as reflected in k_2) as the substituent becomes more electron-withdrawing (increasing σ) as can be seen in Table I. A linear least-squares plot of log k_2 *versus* σ yields slopes of –0.60 for the sulfides and –0.67 for the sulfoxides, values which indicate a very similar relationship between k_2 and σ for these ligands despite the large difference in the reactivities of the two sets of compounds.

A similar trend has also been reported in a study in which a series of substituted diphenylsulfides was reacted with this same substrate [18], a few representative values of which are listed in Table I. From these values it can be seen that replacing a methyl group with a phenyl lowers the reactivity by a factor of 6–10X, presumably becuase of the greater inductive influence of the second phenyl relative to the methyl. The slope of the linear least squares plot of the data from this study (–0.66) is virtually identical with the values from the current work, showing a common dependence of the reactivities of all three series of ligands on the nature of the ring substituent regardless of the identity of the other group on the sulfur or even the presence of the oxygen atom. Finally, the low basicities of the sulfoxides which are reflected in the smaller k_2 values may explain the inability to isolate solid $Ptpy_2L_2^{2+}$ salts with any of the anions employed (Cl^-, ClO_4^-, tosylate$^-$) in contrast to the neutral PtL_2Cl_2 which are readily obtained (although as mixtures of the *cis* and *trans* isomers) [19].

Acknowledgement

The authors express their gratitude to the American Cancer Society for partial support of this work under grant CH-93A and to the Johnson Matthey Company for a generous loan of potassium tetrachloroplatinate.

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