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Nucleophilic Square-planar Substiutitons. IV. The Reaction of Thioethers with Halogenodiethylenetriamineplatinum(II) Cations in Aqueous Ethanol

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Received March 15, 1971

The second-order rate constants for the direct replacement of halogens in halogenodiethylenetriamineplatinum(II) cations by dimethyl sulphide have been determined and the activation parameters calculated. The relative ease of replacement of the outgoing groups are found to follow the order $Cl<Br<I$, a pattern which depends entirely on activation entropy. The results are discussed in terms of an associative mechanism involving the formation of a five-coordinated intermediate, with the second transition state rate-limiting. For the bromo complex, the kinetic studies are extended to di–butyl sulphides and the results provide further support for the associative mechanism.

Introduction

The nucleophilicity of thioethers towards neutral platinum(II) complexes has been studied by Cattalini *et al.*[1] using substrates of the type $[Pt(bipy)CX]$, where the outgoing group X is either Cl, NO_2 or N_3. These results were discussed in terms of an association between the substrate and the nucleophile to produce a five-coordinated intermediate, which then dissociates to give the final product. In order to investigate the behaviour of cationic complexes as substrates and other halogens as outgoing groups towards these nucleophiles, as well as to further distinguish between the dissociation of the intermediate and that of the initial complex, we now report our results for the substitution of halogenodiethylenetriamineplatinum(II) cations by dialkyl sulphides:

$$[Pt(dien)X]^{+}+R_2S \rightarrow [Pt(dien)R_2S]^{2+}+X^{-}$$

Experimental Section

Materials. Chlorodiethylenetriamineplatinum(II) chloride, bromodiethylenetriamineplatinum(II) bromide, and iododiethylenetriamineplatinum(II) iodide were prepared by methods similar to those previously described in the literature,[2,3] and were purified by recrystallisation from water. The dialkyl sulphides, supplied commercially, were shaken with mercuric oxide (to remove mercaptans), dried over anhydrous calcium chloride and fractionally distilled.

Products. The products of the reaction between halogenodiethylenetriamineplatinum(II) cations and thioethers are the corresponding $[Pt(die)R_2S]^{2+}$ cations. Their characterisation may be exemplified by the preparation of the diethyl sulphide complex in the form of the perchlorate salt as described below. To a solution of bromodiethylenetriamineplatinum(II) bromide (0.84×10^{-3} kg) in water (60 cm^3), two equivalents of silver perchlorate were added. The mixture was heated with stirring on a steam bath for half an hour, and the precipitated silver bromide was filtered off. An excess of diethyl sulphide (5×10^{-3} kg) was added to the filtrate at room temperature, ethanol being introduced to bring the mixture into a homogeneous phase. After three days, the mixture was evaporated to a small bulk and the crystals obtained were filtered off, washed with ethanol and then purified by recrystallisation from water. Found: C, 16.71; H, 4.18; N, 6.81; Cl, 12.5%. Calcd for $[Pt(dien)Et_2S](ClO_4)_2$: C, 16.35; H, 3.92; N, 7.16; Cl, 12.1%).

In all cases, the conductance of an aqueous solution the thioether product complex confirms the presence of a 1:2 electrolyte. The analogous compounds $[Pt(NH_3)_3R_2S]^{2+}$ where R = Me and Et, have been reported in literature.[4]

Kinetics. Since the thioethers are insoluble in pure water and the platinum(II) cations are insoluble in pure ethanol, the kinetics were studied in 58% v/v aqueous ethanol in which both nucleophiles and complexes are sufficiently soluble. Runs were carried out with about 0.1 mmole dm^{-3} complex and varying large excess of thioether so that the reaction proceeded virtually to completion and pseudo first-order kinetics were observed for each concentration of the nucleophile. The reaction was followed by a conductance method, whereby solutions of the appropriate complex and of thioether were made up separately to the desired concentrations and placed in a conventional thermostat. When temperature equilibrium had been reached, the solutions were mixed and the resistance measured at intervals in conventional cells kept

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[1] L. Cattalini, M. Martelli, and G. Kirschner, *Inorg. Chem.*, *7*, 1488 (1968).

[2] F.G. Mann, *J. Chem. Soc.*, 466 (1934).

[3] G.W. Watt and W.A. Cude, *Inorg. Chem.*, *7*, 335 (1968).

[4] Gmelins Handbuch der Anorganischen Chemie, Teil D, System Number 68, p. 138 (1957).

Table I. Kinetic data for the direct replacement of X from $[Pt(dien)X]^{2+}$ by R_2S in 58% v/v aqueous ethanol.

Cl	R	k_2 (at 298.2 K) (cm^3 mol^{-1} s^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J K^{-1} mol^{-1})
X	CH_3	13.1	50	—113
Br	CH_3	37.1	50	—109
I	CH_3	55.6	50	—104
Br	n-C_4H_9	4.0	67	— 63
Br	n-C_4H_9	*a*	a	*a*

[a] No observable reaction under identical conditions.

at the required temperature by the thermostat. The observed pseudo first-order rate constants (k_{obs}) were obtained from the semilogarithmic plots of $\log[R_t/(R_t-R_\infty)]$ against time, where R_t is the resistance of the solution at time t and R_∞ is the corresponding value after ten half-lives of the reaction. When these constants were plotted against the concentration of nucleophile, straight lines were obtained which pass virtually through the origin (exemplified in Figure 1). From the slopes of these plots, the second-order rate constants (k_2) for the direct replacement of halogens in halogenodiethylenetriamineplatinum(II) cations by thioetheres may be obtained. The kinetic results are summarised in Table I.

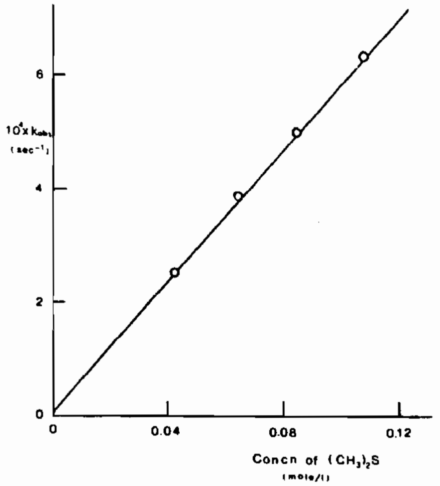

Figure 1. Dependence of observed pseudo first-order rate constants on concentrations of nucleophile for the substitution of the chlorodiethylenetriamineplatinum(II) cation by dimethyl sulphide in 58% v/v aqueous alcohol at 287.2 K.

Discussion

The present results may be discussed in terms of an associative mechanism. In this mechanism (see Figure 2), the nucleophile Y approaches the initial complex (dsp^2) and forms a full bond by using the vacant 6 p_z orbital to give the first transition state (dsp^2+p) which has a square pyramidal structure, with the nucleophile at the apex. Since the filled 5 d_{z^2} orbital also projects in this direction of nucleophilic attack, a relatively more stable intermediate is formed by some rearrangement in which both the Pt—X and the Pt—Y bonds move simultaneously at right angles to the xy plane, giving rise to a trigonal bipyramidal structure (dsp^3). Subsequent movements lead to the second transition state (dsp^2+p) with the outgoing group X now at the apex of another square pyramid and occupying the 6 p_z orbital. The final complex (dsp^2) is then formed by the departure of X. Two types of reaction coordinate diagrams are possible, depending on the relative energy levels of the two transition states, (the third possibility where both transition states are of he same energy applies only to isotopic exchange reactions, for which X and Y are chemically identical). According to Langford and Gray,[5] T.S.2 will be higher in energy than T.S.1 if Y has a smaller *trans*-effect than X, and *vice versa.*

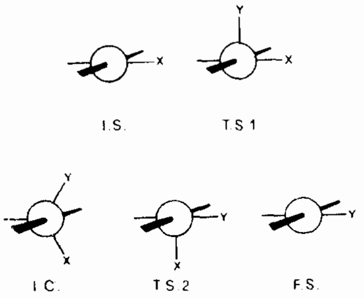

Figure 2. Sequence of rearrangements for nucleophilic substitutions of platinum(II) complexes by an associative mechanism. (I.S. = initial state; T.S. = transition state; I.C. = intermediate complex; F.S. = final state).

In the present reaction, the nucleophile Y is a thioether, the sulphur atom of which is known[6] to be reluctant to form $d_\pi-d_\pi$ bonds with transition metals. Such unimportance of π interaction between sulphur and platinum atoms is supported kinetically by Cattalini *et al.*[1] who showed that for a given substrate a linear plot of log k_2 against the sum of the Taft σ^* values for various thioethers was obtained, with both alkyl and aryl sulphides lying in the same straight line. Consequently, the *trans*-effects of thioethers are expected to be considerably smaller than that of the iodide ion at least, if not also for the bromide and the chloride ions. For the latter two cases, the electron deficiency which is sustained at the platinum atom by the electronegativity of the halogen X (in the order Cl>Br>I) attached in the I.S. is responsible for lowering the energy level of T.S.1 relative to T.S.2. These considerations led us to believe that, for the reaction of thioethers with halogenodiethylene-

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(5) C.H. Langford and H.B. Gray, « Ligand Substitution Processes », W.A. Benjamin, Inc., New York, p. 47 (1965).

(6) R. Backhouse, M.E. Foss, and R.S. Nyholm, *J. Chem. Soc.*, 1714 (1957).

triamineplatinum(II) complexes, T.S.2 is higher in energy than T.S.1, and is therefore rate-limiting. This transition state (T.S.2) leads to the dissociation of the intermediate complex by rupture of the bond between the metal and the halogen. Such a process is governed mainly by bond dissociation energies, giving a rate order of $Cl<Br<I$. Reference to Table I shows that this rate pattern is indeed observed, and that it arises entirely from the entropy of activation varying in the order $Cl<Br<I$. An opposite rate order ($Cl>Br>I$) was observed when pyridine was the entering group[7] so that these results seem to provide a nice example of the symbiotic effect, *i.e.*, I^- stabilizes the five-cordinated intermediate when a soft base such as R_2S is used as nucleophile.

The present discussion is based on a bimolecular mechanism with the second transition state (dissociation of the I.C.) rate-limiting for the thioether substitutions of platinum(II) complexes. The reactivity pattern obtained ($Cl<Br<I$) is similar to that for unimolecular reactions which involves dissociation of the I.S. The only difference probably lies in the greater spread of the rate pattern for the latter. It is therefore necessary to further distinguish between the two mechanisms by considering the steric effects on the reaction, using di–n–butyl and di–tert–butyl sulphides. In general, unimolecular reactions proceed *via* an intermediate of lower coordination number, and is therefore characterised by steric acceleration. Bimolecular reactions on the other hand exhibit steric retardation, due to the formation of an intermediate of higher coordination number. The data collected in Table I shows that for the bromo complex, there is a 9-fold decrease in rate when the nucleophile is changed from dimethyl to di–n–butyl sulphide, while virtually no reaction was observed with di–tert–butyl sulphide where steric hindrance was considerable. These results confirm a bimolecular (associative) mechanism for thioether substitutions of platinum(II) complexes. The effect of the steric retardation is to raise the energy-barrier (T.S.1) for the formation of the I.C. from the I.S. arising from the approach of a bulky thioether Y to the platinum. Since the reaction coordinate diagram is the same for reaction in either direction, T.S.2 will likewise be raised, corresponding to the energy-barrier for the formation of the I.C. from the F.S. arising from the approach of X to a congested site in the vicinity of the bulky thioether Y. Consequently, T.S.2 remains rate-limiting and is responsible for observed higher value of ΔH^* for the reaction with di–n–butyl sulphide.

Acknowledgment. We thank the Committee on Higher Degrees and Research Grants of the University of Hong Kong for financial assistance.

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(7) F. Basolo, H.B. Gray, and R.G. Pearson, *J. Am. Chem. Soc.*, *82*, 4200 (1960).