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KINETICS AND MECHANISM OF ISOMERISATION OF (TRICHLOROETHYLENE)BIS(TRIPHENYLPHOSPHINE)PLATINUM(0) TO CHLORO(DICHLOROVINYL)BIS(TRIPHENYLPHOSPHINE)PLATINUM(II)

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SUMMARY

The kinetics of isomerisation of the olefin complex $Pt(CHCl{=}CCl_2)(PPh_3)_2$ to the vinyl complex *cis*-$PtCl(CH{=}CCl_2)(PPh_3)_2$ have been studied in a range of solvents. The mechanism of this isomerisation has characteristics intermediate between those of a simple intramolecular process and of rate-determining S_N1 loss of chloride from the olefin ligand. This behaviour contrasts with that of the analogous complex $Pt(CCl_2{=}CCl_2)(PPh_3)_2$, where isomerisation occurs almost entirely by the latter route.

INTRODUCTION

We are currently investigating the kinetics and mechanism of isomerisation of complexes of the type (chloroolefin)(phosphine)$_2$platinum to *cis*-chloro(chlorovinyl)(phosphine)$_2$platinum. There are five main variables: (*i*) nature of the chloroolefin; (*ii*) nature of the phosphine (phosphite etc.); (*iii*) nature of the metal; (*iv*) effects of added ligands, *e.g.* chloride; (*v*) solvent.

An investigation of (*iv*) and (*v*) for the complex $Pt(CCl_2{=}CCl_2)(PPh_3)_2$ has been reported[1]. The mechanism of this isomerisation, in hydroxylic solvents, is close to rate-determining S_N1(lim) solvolysis of the tetrachloroethylene ligand followed by platinum–chloride bond formation and platinum–carbon bond rearrangement. In the present paper we deal with variable (*i*) of the above list; results are presented for isomerisation of $Pt(CHCl{=}CCl_2)(PPh_3)_2$ and compared with those for isomerisation of $Pt(CCl_2{=}CCl_2)(PPh_3)_2$ under similar conditions.

RESULTS AND DISCUSSION

The isomerisation of $Pt(CHCl{=}CCl_2)(PPh_3)_2$ follows first-order kinetics until well over 50% of the reaction is complete. Rate constants in a series of solvents are listed in Table 1. This Table also includes Brownstein S values[2] for the solvents. These S values, like Grunwald and Winstein Y values[3], are an empirical measure of the solvating power of the solvent. Grunwald and Winstein's $m \cdot Y$ scales are based solely on reactivity studies; Brownstein's $R \cdot S$ scales are based on thermodynamic and spectroscopic correlations as well.

TABLE 1

AVERAGE FIRST-ORDER RATE CONSTANTS (k) FOR ISOMERISATION OF $Pt(C_2HCl_3)(PPh_3)_2$ IN VARIOUS SOLVENTS, OF SOLVATING POWER S, AT 20.0°

Solvent	S	10^3k (sec^{-1})
MeOH	+0.050	14
EtOH	0	4.4
n-PrOH	−0.016	3.3
iso-PrOH	−0.041	1.6
tert-BuOH	−0.105	0.15
CH_3COOH	+0.005	4.6

For solvolyses:

$$\log_{10}(k/k_0) = m \cdot Y \quad \text{or} \quad R \cdot S$$

where k is the rate constant in a given solvent, k_0 is the rate constant in a reference solvent whose Y or S value is set arbitrarily as zero, and m and R are parameters characteristics of the compound which are again fixed by reference to an arbitrary compound. The plots of the logarithms of the first-order rate constants for the isomerisation of $Pt(CHCl{=}CCl_2)(PPh_3)_2$ against solvent Y or S values are fairly good straight lines; the plot against S values is illustrated in Fig. 1. The values of m and R for the isomerisation of $Pt(CHCl{=}CCl_2)(PPh_3)_2$ have been estimated from this type of graph and are listed (Table 2) together with the values for the standard reference *viz.* S_N1(lim) solvolysis of tert-butyl chloride*.

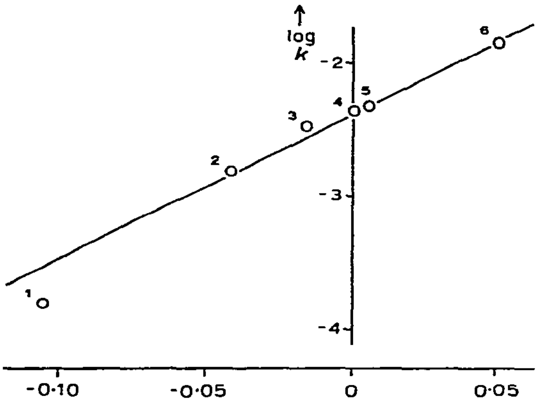

Fig. 1.

TABLE 2

VALUES OF m AND R FOR ISOMERISATION OF CHLOROOLEFIN COMPLEXES OF PLATINUM

Compound	m	R
$Pt(C_2HCl_3)(PPh_3)_2$	0.6	10
$Pt(C_2Cl_4)(PPh_3)_2$	0.9	18
cf. tert-BuCl	1.0	36

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* The fact that rate constants have been determined at temperatures a few degrees from those for which solvent S and Y values are tabulated is not significant since S and Y values change little with temperature[3].

The two mechanisms for isomerisation of the tetrachloroethylene complex, $Pt(CCl_2{=}CCl_2)(PPh_3)_2$, to *cis*-$PtCl(CCl{=}CCl_2)(PPh_3)_2$ which are consistent with preparative[4] and kinetic[1] data are a synchronous intramolecular process and a rate-determining ionisation to $[Pt(CCl{=}CCl_2)(PPh_3)_2]^+$ and Cl^-, possibly associated as an ion-pair, followed by rapid formation of a platinum to chlorine bond and platinum to carbon σ-bond. We have previously shown that the m value of 0.9 for the isomerisation of $Pt(CCl_2{=}CCl_2)(PPh_3)_2$ is more consistent with the latter ionic mechanism. However, the much lower values of m and R for the isomerisation of the trichloroethylene complex $Pt(CHCl{=}CCl_2)(PPh_3)_2$ indicates that the intramolecular process plays a much more important role in the mechanism of this isomerisation.

The rate of isomerisation of $Pt(CHCl{=}CCl_2)(PPh_3)_2$ is considerably faster than that of $Pt(CCl_2{=}CCl_2)(PPh_3)_2$. For example the first-order rate constants for these complexes in ethanol at 35° are $1.9 \times 10^{-2}\,sec^{-1}$ (estimated from Table 3) and $5.4 \times 10^{-5}\,sec^{-1}$, respectively. These values correspond to a difference in free energy of activation of 3.6 kcal·mole^{-1}. The activation parameters for isomerisation of $Pt(CHCl{=}CCl_2)(PPh_3)_2$ in ethanol, calculated from the rate constants reported in Table 3, are $\Delta H^{\ddagger} = 17.6\ (\pm 1.0)$ kcal·mole^{-1} and $\Delta S^{\ddagger} = -10 \pm 4$ e.u. The corresponding values for the tetrachloroethylene complex are $\Delta H^{\ddagger} = 21.4\ (\pm 1.0)$ kcal·mole^{-1} and $\Delta S^{\ddagger} = -9 \pm 4$ e.u. Hence the difference in reactivity here, like the difference in reactivity for the tetrachloroethylene complex in a range of solvents[1], is primarily an enthalpy rather than an entropy effect.

TABLE 3

AVERAGE FIRST-ORDER RATE CONSTANTS (k) FOR ISOMERISATION OF $Pt(CHCl{=}CCl_2)(PPh_3)_2$ IN ETHANOL

Temp. (°C)	10^3k (sec^{-1})
13.0	1.99
15.0	2.26
20.0	4.4
25.0	7.1
30.0	10.8

Due to the low solubility of the vinyl *cis*-$PtCl(C_2HCl_2)(PPh_3)_2$ we have been unable to determine the position of the hydrogen atom in the vinyl group by ^1H NMR. However, this *cis*-vinyl complex can be isomerised[5] to the more soluble *trans*-complex, *trans*-$PtCl(C_2HCl_2)(PPh_3)_2$ to which we have tentatively assigned the structure *trans*-$PtCl(CH{=}CCl_2)(PPh_3)_2$[4]. Recently[6] the ^1H NMR spectrum of the corresponding *trans*-palladium complex has shown it to have the same structure, *trans*-$PdCl(CH{=}CCl_2)(PPh_3)_2$ and since the vinylic hydrogens of both complexes appear at very similar positions in the NMR spectra this further substantiates the structure of the *trans*-platinum complex as *trans*-$PtCl(CH{=}CCl_2)(PPh_3)_2$. Hence it seems reasonable to formulate the *cis*-isomer as *cis*-$PtCl(CH{=}CCl_2)(PPh_3)_2$.

The increased rate of isomerisation of the trichloroethylene complex as compared to the tetrachloroethylene complex is probably due in part to the different electronegativities and consequent inductive effects of hydrogen and chlorine. Thus chloride would be expected to leave a carbon atom more readily when hydrogen is attached to it as is the case in $Pt(CHCl{=}CCl_2)(PPh_3)_2$. Also since olefin complexes of this type are known to be stabilised by electron withdrawing substituents it would be expected that tetrachloroethylene would form stronger bands with platinum than trichloroethylene. Thus since in the isomerisation process part of the olefin breaks away from the platinum it seems reasonable that the tetrachloroethylene complex would isomerise more slowly. However, since trichloroethylene binds quite strongly to platinum in this complex we have not been able to displace it with tetrachloroethylene in order to verify this point.

EXPERIMENTAL

The preparation of the trichloroethylene complex[5] and the techniques used[1] have been described. All solvents were AnalaR grade. The initial concentration of $Pt(CHCl{=}CCl_2)(PPh_3)_2$ was 10^{-4} *M* in all runs.

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