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THE MECHANISM OF ISOMERISATION OF (TETRACHLOROETHYLENE)BIS(TRIPHENYLPHOSPHINE)PLATINUM(0) TO CHLORO(TRICHLOROVINYL)BIS(TRIPHENYLPHOSPHINE)PLATINUM(II)

W. J. BLAND, J. BURGESS AND R. D. W. KEMMITT
Chemistry Department, University of Leicester, Leicester LEI 7RH (Great Britain)

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SUMMARY

The kinetics of isomerisation of the olefin complex $(PPh_3)_2Pt(C_2Cl_4)$ to the vinyl complex $(PPh_3)_2PtCl(CCl{=}CCl_2)$ in ethanol have been investigated and activation parameters determined. Mechanisms which include loss of a triphenylphosphine or a tetrachloroethylene ligand as an initial step are not consistent with kinetic and preparative data. Isomerisation takes place by a completely intramolecular mechanism, through a carbonium ion intermediate, or by a route with characteristics between these two limiting mechanisms.

Recently we have shown that isomerisation of the olefin complex (tetrachloroethylene)bis(triphenylphosphine)platinum(0), $(Ph_3P)_2Pt(C_2Cl_4)$, to the vinyl complex *cis*-chloro(trichlorovinyl)bis(triphenylphosphine)platinum(II), *cis*-$(Ph_3P)_2PtCl(CCl{=}CCl_2)$, is strongly solvent dependent. Thus although no isomerisation occurs in refluxing benzene, acetone, or methylene chloride, addition of ethanol, tetrachloroethylene, or tetracyanoethylene to a benzene solution of the olefin complex results in the formation of the vinyl complex[1]. In the present paper we describe some studies of the mechanism of this isomerisation in ethanol.

RESULTS AND DISCUSSION

The initial rates of reaction in 98% ethanol* are proportional to the initial concentration of the olefin complex over the range 5.0 to 20.0×10^{-5} *M*. Moreover the plots of logarithms of concentration of olefin complex *vs.* time are straight over at least 70% of complete reaction. Thus the isomerisation follows simple first-order kinetics; the calculated rate constants are listed in Table 1.

First-order rate constants for the isomerisation in 98% ethanol at various temperatures are reported in Table 2. From these values activation parameters $\Delta H^{\neq} = 21.4 \pm 1.0$ kcal·mole^{-1} and $\Delta S^{\neq} = -9 \pm 4$ e.u. have been calculated. This value of $\Delta S^{\neq}$ suggests that $\Delta V^{\neq}$ for the isomerisation is also small and negative[2].

The reaction rates decrease smoothly as the proportion of ethanol in ethanol/

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* Reaction mixtures contained 2% dichloromethane; see *Experimental*.

TABLE 1

FIRST-ORDER RATE CONSTANTS (k_1) FOR ISOMERISATION OF $(PPh_3)_2Pt(C_2Cl_4)$ IN ETHANOL AT 35.0°

Initial $[(PPh_3)_2Pt(C_2Cl_4)] \times 10^5$ (M)	10^5k_1 (sec^{-1})
5.0	5.2
7.5	5.6
10.0	5.0
12.5	5.6
15.0	5.4
17.5	5.9
20.0	5.1

dichloromethane solvent mixtures decreases (Table 3). The olefin complex has a half-life of several days in solution in dichloromethane at 35.0°.

There are several possible mechanisms for this isomerisation which are consistent with the observed first-order kinetics:

1. intramolecular;
2. loss of a triphenylphosphine ligand, rearrangement of the intermediate, and recombination with triphenylphosphine;
3. loss of the tetrachloroethylene ligand, followed by recombination and fission of this ligand so that one carbon and one chlorine become attached to the platinum;
4. loss of chloride from the tetrachloroethylene ligand, followed by rearrangement of the carbonium ion and nucleophilic attack of the chloride at platinum.

These are limiting mechanisms; the actual isomerisation may well take place by some intermediate mechanism.

In mechanisms 2, 3, and 4 either (*a*) initial ligand or chloride loss, or (*b*) a subsequent step, may be rate-determining. In case (*a*) activation parameters can be discussed in terms of a simple unimolecular model for the first step, but it would be difficult to obtain kinetic information on subsequent stages of the mechanism. In case (*b*) discussion of the activation parameters would be complicated by the incorporation of the thermodynamic parameters for the initial equilibrium into the measured activation parameters. However, addition of triphenylphosphine, tetra-

TABLE 2

FIRST-ORDER RATE CONSTANTS (k_1) FOR ISOMERISATION OF $(PPh_3)_2Pt(C_2Cl_4)$ AT VARIOUS TEMPERATURES

Temperature (°C)	10^5k_1 (sec^{-1})
35.0	5.4[a]
40.0	9.5[b]
45.0	16.6[b]
50.0	28.5[b]

[a] Mean value from Table 1. [b] Mean result from three separate kinetic runs.

TABLE 3

VARIATION OF FIRST-ORDER RATE CONSTANT (k_1) FOR ISOMERISATION OF $(PPh_3)_2Pt(C_2Cl_4)$ WITH ETHANOL/DICHLOROMETHANE SOLVENT COMPOSITION AT 35.0°

Ethanol (Volume %)	10^5k_1 (sec^{-1})
98	5.4[a]
78	5.4
58	3.7
38	2.2

[a] Mean of values in Table 1.

chloroethylene, or chloride might affect both concentrations and rates of reaction of intermediates, therefore the effects of such additions on isomerisation rates may yield further information. There are too many variables for an unequivocal assignment of mechanism to be made on the basis of available data, but some of the mechanisms outlined above can be eliminated.

If in mechanism 2 the initial equilibrium is relatively rapidly established and is followed by slow rearrangement of the intermediate, then addition of triphenylphosphine should retard the overall isomerisation rate by forcing the initial equilibrium to the left-hand side. The rate constants reported in Table 4 show negligible retardation of rate in the presence of added triphenylphosphine, hence this variant of the isomerisation mechanism is inadmissible*. Alternatively loss of triphenylphosphine from the olefin complex could be slow and rate-determining. The formation of the transition state for this reaction involves stretching the platinum to phosphorus bond, which as the ligand is neutral, will not generate a significant dipole. Thus only a small change in solvation, and thus a small value of $\Delta S^{\neq}$, would be expected. This is consistent with our kinetic results. However if the general correlation of entropies and volumes of activation[2] does apply in this particular reaction, then the small and negative value of $\Delta V^{\neq}$ guessed from $\Delta S^{\neq}$ for this isomerisation is not consistent with the appreciable and positive value of $\Delta V^{\neq}$ expected for the unimolecular rate-determining step postulated in this variant of mechanism 2.

TABLE 4

EFFECT OF ADDED TRIPHENYLPHOSPHINE ON FIRST-ORDER RATE CONSTANTS (k_1) FOR ISOMERISATION OF $(PPh_3)_2Pt(C_2Cl_4)$ AT 50.0°

$[PPh_3]$ added/ initial $[(PPh_3)_2Pt(C_2Cl_4)]$	10^5k_1 (sec^{-1})
0	28
1.0	26
2.5	25

When the olefin complex isomerises in the presence of tetracyanoethylene (TCNE), no TCNE is incorporated into the vinyl product. It is known that tetrachloroethylene does not displace TCNE from $(PPh_3)_2Pt(TCNE)$[1]. Thus mechanism 3 is inconsistent with preparative data, despite the plausibility of $(PPh_3)_2Pt$ as an intermediate[3].

Two likely mechanisms remain, 1 and 4, and these differ only in the degree of freedom enjoyed by the chloride at intermediate stages of the reaction. Incorporation of ethoxide into the vinyl product would have furnished positive evidence for mechanism 4, the observed lack of incorporation can be interpreted by mechanism 1 or 4. The effect of added chloride on isomerisation rates yields no positive evidence, for reasons already outlined for tetrachloroethylene. The activation parameters for the isomerisation are in the range observed for S_N1 solvolysis reactions of alkyl

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* It was not possible to add any larger excess of triphenylphosphine because of its large absorption in the region of the ultra-violet in which measurements had to be made (*cf.* Experimental), but as the initial equilibrium lies well to the left the amount of triphenylphosphine added was very much larger than that which would be in equilibrium with the olefin complex in the absence of added triphenylphosphine.

halides and therefore consistent with mechanism 4. But the fairly large activation enthalpy is also consistent with stretching platinum–carbon and carbon–chlorine bonds in the transition state for intramolecular isomerisation (mechanism 1), while the small activation entropy is consistent with a small difference in solvation between initial and transition states for this mechanism. The variation of rate with ethanol concentration (Table 3) implies stronger interaction of ethanol than of dichloromethane with the olefin complex. This rate variation may arise primarily from solvation of a leaving chloride ion (mechanism 4) or from more general solvation of the complex, and indeed does not distinguish between any of the four suggested mechanisms.

It is apparent from the foregoing discussion that it has not proved possible to obtain sufficient kinetic and preparative data to discriminate between all possible mechanisms for this isomerisation. We hope to clarify the situation by studying kinetic and preparative aspects of this and related isomerisation reactions both in a variety of solvents and in the presence of a variety of added ligands.

EXPERIMENTAL

(Tetrachloroethylene)bis(triphenylphosphine)platinum was prepared as described earlier. It was purified by recrystallisation from acetone; acetone was removed from the crystals *in vacuo* at 60°. Solutions of the complex were prepared in dichloromethane; these were stable for several days at room temperature. Tetrachloroethylene was redistilled, and triphenylphosphine recrystallised from ethanol, before use.

The olefin complex has $\lambda_{max} = 230$, 252 mμ; the vinyl complex has $\lambda_{max} = 228$ mμ. Absorbance readings in the kinetic runs were made at 288 mμ; at this wavelength the vinyl complex has negligible absorption while the olefin complex still absorbs fairly strongly as the 252 mμ peak is broad and has a shoulder at about 275 mμ.

Kinetic runs were conducted in 1 cm cells in the thermostatted cell compartment of either a Unicam SP800A or a Beckman DB-G spectrophotometer. In all cases a run was started by adding 0.05 ml of a solution of $(PPh_3)_2Pt(C_2Cl_4)$ in dichloromethane to 2.45 ml of ethanol, ethanol/dichloromethane mixture, or ethanol solution of an appropriate ligand. The results quoted in Table 2 indicate that the presence of 2% by volume dichloromethane makes no difference to the isomerisation rates of $(PPh_3)_2Pt(C_2Cl_4)$ in ethanol. The initial concentration of $(PPh_3)_2Pt(C_2Cl_4)$ was 10^{-4} M in all runs whose results are reported in Tables 2 to 4.

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