

SOLVENT EFFECTS ON THE KINETICS OF ISOMERISATION OF (TETRACHLOROETHYLENE)BIS(TRIPHENYLPHOSPHINE)PLATINUM(0) TO CHLORO(TRICHLOROVINYLBIS(TRIPHENYLPHOSPHINE)-PLATINUM(II)

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SUMMARY

The kinetics of isomerisation of the olefin complex $(PPh_3)_2Pt(C_2Cl_4)$ to the vinyl complex $(PPh_3)_2PtCl(CCl=CCl_2)$ have been studied in a variety of single and mixed solvents. The dependence of rates on ionising powers of solvents indicates that the rate-determining step, in hydroxylic solvents, is close to $S_N1(lim)$ solvolysis of the tetrachloroethylene ligand, involving a carbonium ion intermediate, $(PPh_3)_2Pt-(C_2Cl_3)^+$. The mechanism of the isomerisation is somewhat different in benzene.

INTRODUCTION

We have recently reported an investigation of the isomerisation of (tetrachloroethylene)bis(triphenylphosphine)platinum(0), $(PPh_3)_2Pt(C_2Cl_4)$, to chloro(trichlorovinyl)bis(triphenylphosphine)platinum(II), $(PPh_3)_2PtCl(CCl=CCl_2)$, in ethanol solution¹. The mechanism was found either to be intramolecular, to involve intermediate formation of a carbonium ion, or to combine the characteristics of these two extremes. We have now determined isomerisation rates, and in some cases activation parameters, in a variety of single and mixed solvents. In the following discussion it is shown that the correlation of rates with ionising powers of solvents² indicates that isomerisation proceeds through a carbonium ion intermediate, at least in alcohols and acetic acid.

RESULTS AND DISCUSSION

For a variety of unimolecular reactions conducted in a variety of single and mixed solvents it has been shown that the rate constant (k) for reaction in a particular solvent can be related to the rate constant (k_0) in a standard solvent by the expression^{3,4}:

$$\log_{10} \frac{k}{k_0} = mY$$

where Y is a parameter characteristic of the solvent, often somewhat loosely described as the "ionising power" of the solvent, and m is characteristic of the compound. The

TABLE 1

AVERAGE FIRST-ORDER RATE CONSTANTS (k) FOR ISOMERISATION OF $(PPh_3)_2Pt(C_2Cl_4)$ IN SOLVENTS OF VARYING IONISING POWER (Y), AT 35.0°

Solvent	10^5k (sec^{-1})	Y^a
MeOH	35	-1.09
EtOH	5.4	-2.03
n-PrOH	3.0	-2.30 ^b
iso-PrOH	0.82	-2.73
tert-BuOH	< 0.1	-3.26
$(CH_2OH)_2$	80	-0.45 ^b
CH_3COOH	6.2	-1.68

^a From ref. 5. ^b Estimated from Z and E_T values (cf. text).

arbitrary reference points are taken as $Y=0$ for 80% ethanol, $m=1$ for tert-butyl chloride as a typical compound undergoing solvolysis by a mechanism approximating to $S_N1(lim)$. We have determined first-order rate constants for isomerisation of

TABLE 2

AVERAGE FIRST-ORDER RATE CONSTANTS (k) FOR ISOMERISATION OF $(PPh_3)_2Pt(C_2Cl_4)$ IN METHANOL-WATER MIXTURES, AT 35.0°

% water (v/v)	10^5k (sec^{-1})	Y^a
0	35	-1.09
10	82	-0.30
20	150	+0.38
30	400	+0.96

^a From ref. 5.

(tetrachloroethylene)bis(triphenylphosphine)platinum(0) in a variety of media. Average values are listed in Tables 1, 2, and 3, together with the respective solvent Y values. It should be mentioned that in two cases it has been necessary to estimate Y values from related solvent spectroscopic parameters Z and E_T ; the justification for this can be found elsewhere².

TABLE 3

FIRST-ORDER RATE CONSTANTS (k) FOR ISOMERISATION OF $(PPh_3)_2Pt(C_2Cl_4)$ IN ACETIC ACID-WATER MIXTURES, AT 35.0°

$[H_2O]$ M	10^5k (sec^{-1})	Y^a
0	6.2	-1.68
2.0	30	-0.86
4.0	58	-0.40

^a From ref. 5.

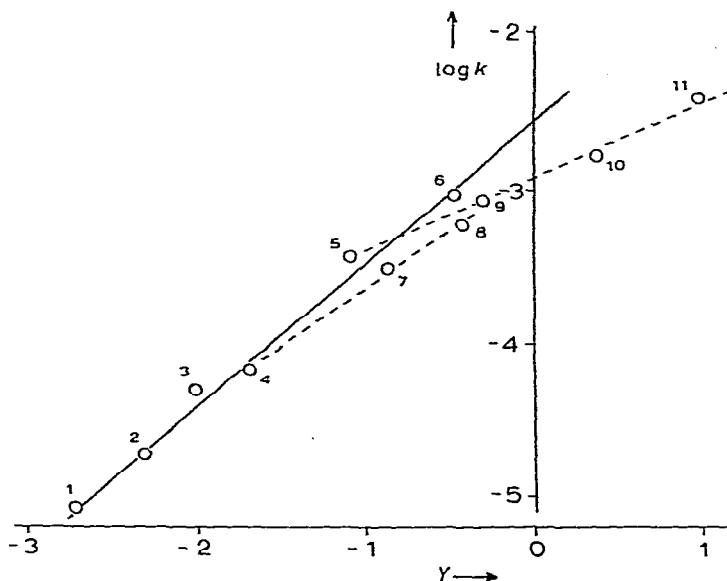


Fig. 1. Graph of logarithms of rate constants (k) for isomerisation of $(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{Cl}_4)$ at 35.0° against solvent Y values. Points: 1, isopropanol; 2, n-propanol; 3, ethanol; 4, acetic acid; 5, methanol; 6, ethylene glycol; 7 and 8, 2 M , 4 M water in acetic acid; 9, 10 and 11, 10%, 20% and 30% water in methanol. Correlation lines: —, single solvents; ---, mixed aqueous solvents.

Logarithms of rate constants have been plotted against Y values in Fig. 1. The points for pure solvents fall on a straight line of slope (m) 0.88. This value is similar to the m values observed for $\text{S}_{\text{N}}1$ solvolysis of typical organic halides. The m values for isomerisation of the chloro-olefin complex in methanol-water and acetic acid-water mixtures are somewhat lower, $m=0.50$ and 0.81 respectively. Some variation of m with type of solvent system is normal behaviour⁶. These results indicate that the first and rate-determining step in isomerisation of the chloro-olefin complex is breaking of a C-Cl bond, with either formation of an ion-pair (contact or solvent-separated), or with liberation of chloride into solution. This first step must be followed by rapid attack of chloride at the platinum and fission of one Pt-C bond to yield the chloro(trichlorovinyl) product. A purely intramolecular mechanism for this isomerisation might also give a linear plot of the logarithm of rate constant against solvent Y value but a slope of nearly one, *i.e.* such a large variation of rate with solvent as is observed, is highly unlikely.

In view of the qualitative observations⁷ that addition of tetrachloroethylene promotes, but addition of triphenylphosphine inhibits, the isomerisation of the chloro-olefin complex in benzene solution we have tried to extend the above treatment to cover these situations. Experimental difficulties have prevented the extension of the Y scale to poorly ionising solvents such as benzene. However, Brownstein⁸ has had considerable success in a more general correlation of spectroscopic, kinetic, and equilibrium data by an expression similar to that given above, *viz.* :

$$\log_{10} \frac{x}{x_0} = RS$$

TABLE 4

AVERAGE FIRST-ORDER RATE CONSTANTS (k) FOR ISOMERISATION OF $(PPh_3)_2Pt(C_2Cl_4)$ AT 50.0°

Solvent	$10^5 k$ (sec^{-1})	S^a
MeOH-aq ^b	430	+0.079
MeOH	120	+0.050
EtOH	29	0
n-PrOH	14	-0.016
iso-PrOH	3.0	-0.041
tert-BuOH	0.2	-0.105
C ₆ H ₆	0.4	-0.215
C ₂ Cl ₄	<0.1	-0.263

^a Values from ref. 8. ^b 80% methanol, 20% water (v/v).

Here x is the frequency, rate, or equilibrium constant for the compound or reaction in a given solvent, x_0 the analogous value in the reference solvent, and R and S are the compound or reaction and the solvent parameters (*cf.* m and Y) respectively. Obviously S values can readily be obtained from spectroscopic data when the corresponding Y values cannot be determined kinetically due to low ionising power of a solvent and its consequent low reactivity. We shall use these S values for a more extensive correlation of rates with solvent properties than was possible for rates and Y values (Fig. 1), though the extrapolation inherent in the use of S values for benzene, tert-butyl alcohol, and tetrachloroethylene is slightly less satisfactory than the interpolation of Y values used in two cases in Table 1. First-order rate constants, at 50.0° , and solvent S values are listed in Table 4; logarithms of these rate constants are plotted against S values in Fig. 2.

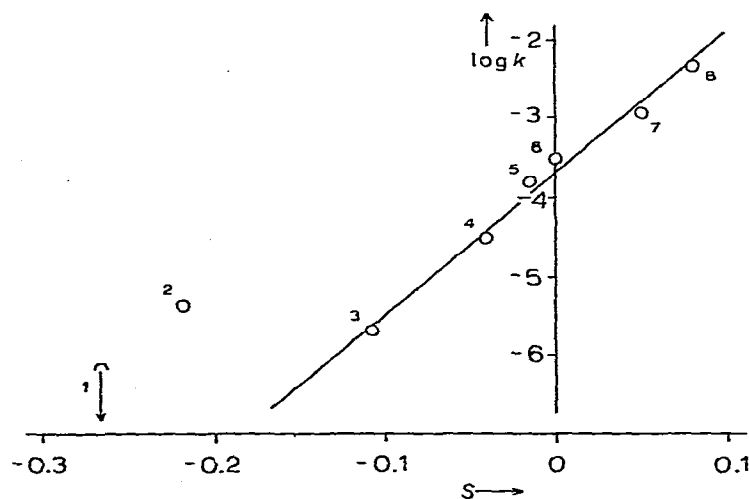
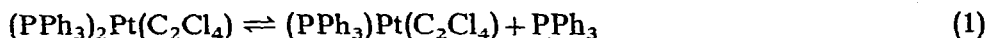


Fig. 2. Graph of logarithms of rate constants (k) for isomerisation of $(PPh_3)_2Pt(C_2Cl_4)$ at 50.0° against solvent S values. Points: 1, tetrachloroethylene (upper limit indicated); 2, benzene; 3, tert-butyl alcohol; 4, isopropanol; 5, n-propanol; 6, ethanol; 7, methanol; 8, 20% water in methanol.

Figure 2 shows that logarithms of rate constants at 50.0° correlate linearly with solvent *S* values, just as logarithms of rate constants at 35.0° did with *Y* values*, for hydroxylic solvents. But the point for benzene is significantly away from the correlation line in Fig. 2; isomerisation takes place several times more rapidly than would have been expected from this correlation line. This suggests that some alternative mechanism makes a significant contribution to isomerisation in benzene solution. It seems likely that triphenylphosphine is strongly solvated in benzene, and that in the following equilibrium:



this strong ligand-benzene interaction may cause some dissociation of the bis-(triphenylphosphine) complex. A chlorine atom of the tetrachloroethylene ligand might then move, as the rate-determining step, to the platinum; subsequent platinum to carbon bond fission followed by equilibrium readdition of triphenylphosphine would then yield the chloro(trichlorovinyl) product. If this mechanism applies, then addition of excess triphenylphosphine should inhibit isomerisation by forcing equilibrium 1 above to the left, as indeed is the case (Table 5).

TABLE 5

EFFECT OF ADDED TRIPHENYLPHOSPHINE ON FIRST-ORDER RATE CONSTANTS (*k*) FOR ISOMERISATION OF $(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{Cl}_4)$, AT 50.0°

[PPh ₃] added Initial [(PPh ₃) ₂ Pt(C ₂ Cl ₄)]	10 ⁵ <i>k</i> (sec ⁻¹)		
	C ₆ H ₆	EtOH	n-PrOH
0	0.4	28	14
0.5	<0.1	28	16
1.0	—	26	19
1.5	<0.1	30	—
2.5	—	25	22

It is of interest to compare the effect on rates of added triphenylphosphine in benzene with that in alcohols. Rate constants determined in ethanol and in n-propanol are listed in Table 5. In the alcohols the mechanism of isomerisation is that of rate-determining intermediate carbonium ion formation (see above); addition of excess triphenylphosphine presumably causes the slight increase of rate in n-propanol solution by some triphenylphosphine-platinum interaction which is transmitted to the breaking carbon-chlorine bond. The larger effect in n-propanol than in ethanol may be explained by greater interaction between platinum and solvent ethanol than between platinum and solvent n-propanol making displacement of the solvating ethanol by triphenylphosphine more difficult. Thus the different effects of added triphenylphosphine on isomerisation rates in alcohols and in benzene are consistent with the suggested differences in mechanism.

The effect of added tetrachloroethylene on isomerisation rates is more difficult

* *S* and *Y* scales actually refer to 25.0°, but temperature differences of 10.0° and of 25.0° as here have a negligible effect³.

to discuss. There is no significant change in rate ($k=4 \times 10^{-6} \text{ sec}^{-1}$) on adding tetrachloroethylene to benzene in ratios of up to 60% (by volume) of the former, though the rate in pure tetrachloroethylene is known to be less than 10^{-6} sec^{-1} . The difference between kinetic and the earlier qualitative⁷ observations must arise from differences in concentrations and temperature between the two sets of experiments rather than from a general rate enhancement by added tetrachloroethylene. However the dependence of rate on solvent composition in benzene-tetrachloroethylene mixtures is not what might be expected from the behaviour in benzene-ethanol mixtures, where the logarithm of the rate constant varies practically linearly with solvent composition.

The remaining source of kinetic information on isomerisation of the chloro-olefin complex is the variation of activation parameters with solvent composition. Rate constants have been determined at 5.0° intervals over the temperature range 35.0 to 50.0° for the single solvents methanol, ethanol, and n-propanol; for one methanol-water mixture, where both components promote reaction; and for two benzene-ethanol mixtures, where the benzene is effectively a neutral diluent. Average experimental rate constants, with the activation parameters calculated from them, are listed in Table 6. Estimated errors in ΔH^\ddagger and ΔS^\ddagger are $\pm 1.0 \text{ kcal-mole}^{-1}$ and $\pm 4 \text{ e.u.}$ respectively.

TABLE 6

AVERAGE FIRST-ORDER RATE CONSTANTS (k), AND ENTHALPIES (ΔH^\ddagger) AND ENTROPIES (ΔS^\ddagger) OF ACTIVATION, FOR ISOMERISATION OF $(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{Cl}_4)$ IN VARIOUS SOLVENTS

Solvent ^a	$10^5 k \text{ (sec}^{-1}\text{)}$				ΔH^\ddagger (kcal·mole ⁻¹)	ΔS^\ddagger (e.u.)
	35.0°	40.0°	45.0°	50.0°		
80% MeOH/20% water	150	208	302	430	13.4	-29
MeOH	35	53	75	116	15.0	-26
n-PrOH	3.0	5.3	8.6	14.6	19.8	-15
EtOH ^b	5.4	9.5	16.6	28.5	21.4	-9
80% EtOH/20% C ₆ H ₆	1.9	3.6	6.5	9.8	21.4	-12
60% EtOH/40% C ₆ H ₆	0.94	1.84	2.86	5.2	20.4	-15

^a Mixed solvent compositions by volume. ^b Data from ref. 1.

A plot of activation entropy against activation enthalpy is reasonably linear, which is the expected behaviour⁸ for a series of reactions in which there is only one significant variable — here solvation of the leaving chloride. Changes in activation enthalpy dominate over changes in activation entropy in determining reaction rates, which is the more usual behaviour. The activation entropy-enthalpy plot indicates an isokinetic temperature, β ,^{*} of around 400°K, which is in the expected region for a solvolysis reaction. Further comment on this value is precluded by the paucity of information on even vaguely related reactions⁹.

* β is defined by $\Delta H^\ddagger = \beta \cdot \Delta S^\ddagger$; it is the temperature at which enthalpy domination of rates gives way to entropy domination.

EXPERIMENTAL

The preparation and purification of the chloro-olefin complex and the techniques used were the same as described earlier¹. All solvents were AnalaR grade. The initial concentration of $(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{Cl}_4)$ was $10^{-4} M$ in all runs.

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