Inorganica Chimica Acta, 65 (1982) L179–L180

Leaving Group Solvation in the Isomerisation of *Cis*-bis-triethylphosphine-*m*-methylphenyl-chloroplatinum(II)

M. J. BLANDAMER, J. BURGESS

Department of Chemistry, University of Leicester, Leicester LE1 7RH, U.K.

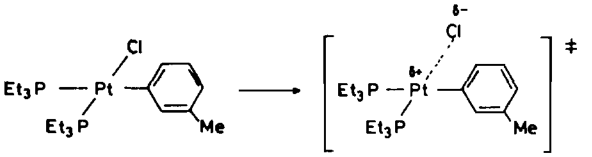
and R. ROMEO

Istituto di Chimica Fisica, Università di Messina, 98100 Messina, Italy

Received June 12, 1982

There has been controversy over the mechanism of isomerisation of *cis*-[Pt(PEt$_3$)$_2$(R)Cl], where R = substituted aryl, with one group presenting a range of evidence in favour of a dissociative mechanism [1–5], another arguing in favour of the more commonly encountered associative mode of activation [6–8]. The purpose of this letter is to present a new line of evidence in favour of the dissociative mechanism by consideration of solvent effects on rate constants and their relation to solvation of the leaving chloride ligand.

In the dissociative mechanism it is believed that the platinum–chloride bond is almost completely broken by the time the transition state is attained:



Electrophilic solvation of the leaving chloride ion through hydrogen bonding is thought to be the major factor in determining the large differences in rates observed for isomerisation of *cis*-[Pt(PEt$_3$)$_2$(*m*-C$_6$H$_4$Me)Cl] in a series of alcohols, the contribution from nucleophilic or non-specific solute–solvent interactions being negligible [5]. In our present discussion we observe that if the mechanism and these assumptions are valid, then solvation changes around the [Pt(PEt$_3$)$_2$(*m*-C$_6$H$_4$Me)] moiety should vary very little on going from the initial to the transition state. Therefore changes in rate constants forecast from changes in chemical potential of chloride ion on transfer between solvents ($\delta_m\mu^\theta(\mathrm{Cl}^-)$) should be closely similar to the changes reported in earlier kinetic studies [5].

Unfortunately no set of Gibbs free energies of transfer for the chloride ion between the various aliphatic monohydroxylic alcohols exists. A range of values for $\delta_m\mu^\theta(\mathrm{Cl}^-)$ for transfer from water into methanol exists, the variation reflecting the various extrathermodynamic assumptions used [9]. The value for $\delta_m\mu^\theta(\mathrm{Cl}^-)$ from water into ethanol [10] uses yet another extrathermodynamic assumption for the single ion split. We are not aware of values of $\delta_m\mu^\theta(\mathrm{Cl}^-)$ for transfer into other aliphatic monohydroxylic alcohols. There are, however, several sets of solubility data for alkali metal chlorides in aliphatic alcohols.

We shall derive values of $\delta_m\mu^\theta(\mathrm{Cl}^-)$ from potassium chloride solubilities reported by Larson and Hunt for a range of alcohols [11]. In the Table we give these solubilities in molarities (densities are included in ref. [11]). Thence we calculate $\delta_m\mu^\theta(\mathrm{KCl})$ for transfer from methanol, using the assumption $\gamma_\pm(\mathrm{ROH})/\gamma_\pm(\mathrm{MeOH}) = 1.00$ for all the alcohols. This assumption seems reasonable in view of the low solubility of potassium chloride in all these alcohols. To split $\delta_m\mu^\theta(\mathrm{KCl})$ into single ion components we use the assumption

$$\delta_m\mu^\theta(\mathrm{Cl}^-) = 0.54\ \delta_m\mu^\theta(\mathrm{KCl})$$

TABLE I. Prediction of $\delta_m\mu^\theta(\mathrm{Cl}^-)$ Values and thence of Relative Rates of Isomerisation of *cis*-[Pt(PEt$_3$)$_2$(*m*-C$_6$H$_4$Me)Cl] in Aliphatic Alcohols.

	$10^3[\mathrm{KCl}]^a$ mol dm^{-3}	$\delta_m\mu^\theta(\mathrm{KCl})^b$ kJ mol^{-1}	$\delta_m\mu^\theta(\mathrm{Cl}^-)^{b,c}$ kJ mol^{-1}	$\log_{10} k(\mathrm{MeOH})/k(\mathrm{ROH})$	
				forecast^d	actual [5]
MeOH	57.2				
EtOH	3.09	+14.5	+7.8	1.30	1.26
1-PrOH	0.66	+22.1	+11.9	1.98	1.71
1-BuOH	0.32	+25.7	+13.9	2.32	2.06
2-PrOH	0.24	+27.1	+14.6	2.43	2.31

^{a}Saturated solution; from ref. [11]. ^{b}Molar calc. ^{c}Assuming $\delta_m\mu^\theta(\mathrm{Cl}^-) = 0.54\ \delta_m\mu^\theta(\mathrm{KCl})$; *cf.* text. ^{d}At 313 K.

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

The factor 0.54 is that indicated from Popovych and Dill's transfer parameters into ethanol [10]. Published data referring to transfer into methanol suggest a short range of values in this region. Our estimates for $\delta_m\mu^\theta(Cl^-)$ are given in Table I. It is reassuring that our estimate for transfer from ethanol into propan-1-ol, +4.1 kJ mol^{-1}, is close to that, +5.4 kJ mol^{-1}, obtained by application of the $AsPh_4^+ \equiv BPh_4^-$ assumption to appropriate experimental data [3, 12].

From our estimated values of $\delta_m\mu^\theta(Cl^-)$ it is a straightforward matter to calculate relative rate constants on the assumption that reactivity trends are determined solely by this transition state contribution. Our kinetic forecasts are given in the Table in the form of $\log\{k(MeOH)/k(ROH)\}$, and compared with the values of this parameter calculated from published kinetic data [5]. There is a remarkable similarity between the forecast and actual values, providing strong support for the hypothesis of a predominantly dissociative mechanism for this isomerisation. In fact the ratios of forecast to actual ratios of rate constants average to about 1.1, suggesting that the platinum-chloride bond is almost broken in the transition state, the incipiently leaving chloride having developed a charge of about 0.9.

For transfer from methanol into acetonitrile, $\delta_m\mu^\theta(Cl^-)$ = +26 kJ mol^{-1} ($AsPh_4^+ \equiv BPh_4^-$ assumptions [13, 14]). Such a value predicts a half-life of about 9 days for isomerisation of *cis*-$[Pt(PEt_3)_2(m\text{-}C_6H_4Me)Cl]$. In practice this reaction is about five times faster [5]. This difference may be attributed to specific interactions between acetonitrile and the platinum compound, though it may be also due in part to the difference in $\delta_m\mu^\theta(Cl^-)$ derivation assumptions.

The limited amount of information in the literature on dissociative processes of this type and the success of the above analysis prompt us to carry out appropriate solubility and kinetic measurements so that we can conduct a full initial state-transition state analysis on some of these isomerisations in a selection of solvent media.

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