Solvent Controlled Anchimeric Assistance in Some Nucleophilic Substitutions at Platinum(II) Square Planar Derivatives

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Kinetics results concerning nucleophilic substitution of chloride from the complexes [Pt(bipy)(am)-Cl]BPh$_4$ (bipy = α,α'-dipyridyl; am = ethanolamine and ethylamine) in methanol and acetonitrile are reported. The second-order kinetic rate constants together with the solubilities of the reactants provide a basis for the calculation of the transfer chemical potentials for initial and transition state of every reported reaction. The kinetic behaviour of the two complexes is very similar in methanol, but in acetonitrile the ethanolamine derivative reacts about 2–3 times faster than the ethylamine derivative. This difference is interpreted on the basis of a solvent-controlled anchimeric assistance which is provided to the leaving chloride by the dangling hydroxo-residue of the ethanolamine only in the aprotic acetonitrile.

Introduction

The kinetic role of the solvent in substitution reactions at square-planar complexes of d^8 transition metal ions still presents a number of complex problems. The reactivity order of the entering ligands, for example, often depends on both the solvent and the leaving group [1–3]. This kind of behaviour is irregular for substitutions at square-planar platinum(II) complexes, where entering ligands can be arranged in order of nucleophilicity, independent of substrate and solvent, resulting in the quantitative n_{Pt} scale. Deviation from this behaviour has been attributed to a high degree of synchronicity of bond-making and bond-breaking in the transition state [4]. In the present paper we report kinetic results concerning the nucleophilic substitution of the chloride from [Pt(bipy)(am)Cl]PPh$_4$ (am = ethanolamine and ethylamine) by Br^- and tu in methanol and acetonitrile at 298 K. Solubilities and rate parameters provide a basis for the calculation of transfer chemical potentials of initial state and transition state for the reported second-order reactions. Our results suggest that a key role in determining the kinetics of the chloride replacement is played by the hydrogen bonding properties of the solvent.

Experimental

Preparation of [Pt(bipy)(am)Cl]BPh$_4$

Pt(bipy)(NH$_2$(CH$_2$)$_2$OH)ClBPh$_4$, (I), was prepared by adding the stoichiometric amount of ethanolamine to a suspension of Pt(bipy)Cl$_2$ in methanol. The reaction mixture, refluxed for one hour, yielded a yellow solution which was cooled and filtered. The pH of this solution was then adjusted to 3–4 with a few drops of a methanolic solution of HCl 1 *M* and the cationic complex precipitated by addition of a solution of NaBPh$_4$ in methanol. The compound was recrystallized from acidic solution (pH = 3–4) of hot methanol.

A similar procedure was used for the preparation of [Pt(bipy)(NH$_2$CH$_2$CH$_3$)Cl]BPh$_4$, complex(II). In this case the addition of HCl was unnecessary.

Kinetics

For all the kinetics pseudo-first-order conditions were assured by an at least seven times excess of nucleophile with respect to the complex. The reactions were followed spectrophotometrically and, when possible, conductometrically.

In the former case methanolic solutions of substrate and nucleophile, whose ionic strength was maintained constant at $\mu = 0.15$ by addition of suitable amounts of LiClO$_4$, were separately brought to the reaction temperature and then mixed in a thermostatted cell of an OPTICA CF4R or CARY 219 double-beam spectrophotometer. In order to shift the ring closing equilibrium which takes place in neutral methanolic solutions of complexes(I) [5] toward the open chain species, we added small amounts of HCl (10^{-4} mol dm^{-3}) to methanolic solutions of complex(I) before mixing in the thermostatted cell of the spectrophotometer. In these conditions the u.v. spectrum was stable and clearly indicated that the open chain form was largely dominant. The rate of the chloride replacement from complex-(II) in methanol was unaffected by the presence of small amounts of HCl, therefore we can reasonably suppose that the hydrochloric acid influences only the ring closing equilibrium of complex(I) without affecting the rate of chloride replacement.

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Acetonitrile solutions of complex(I) are stable, therefore the additions of acid could be avoided. In this solvent, however, the salt effects could not be controlled by working at constant ionic strength as in methanol. This neglect, taking into account the similarity between the dielectric constants of the two solvents and the low concentration of ionic species employed for the kinetic experiments in acetonitrile, should not affect our conclusions in any way.

The kinetic course was monitored at a suitable wavelength in the u.v. region by the absorbance variations associated with the reactions. The observed rate constants, k_{obs}, were evaluated from the gradients of the plots of $\ln|A_\infty - A_t|$ against time, where A_∞ and A_t represent the absorbance after approximately five half-lives and the absorbance at time t, respectively. The rate constants concerning the two stages of the reactions of complexes (I) and (II) with tu were sufficiently different and the observed rate constants relative to the first-stage could be calculated without large uncertainty by Guggenheim's analysis.

The conductometric kinetics were followed by the increase in the conductivity arising from the formation of a 2:1 from a 1:1 charged complex. The solutions of complexes in this case were prepared just before the kinetic use in the neat solvent; under these experimental conditions the rate of the ring closing reaction which takes place in neutral methanolic solution of (I) should, with respect to the chloride replacement by tu, be slow enough to leave the rate of conductivity enhancement nearly unaffected. A Radiometer CDM 3 conductivity bridge equipped with a Rec 61 Servograph recorder was used to monitor the reaction course. A sample of the complex (25 ml) was placed in a vessel in which a conductivity cell was immersed. To these solutions, thermostatted at 25 °C, the nucleophile (0.5 ml) at a suitable concentration was injected under magnetic stirring. The stirring was then suspended and the increase in conductivity was monitored. The experimental c/t curves were linearized by plotting $\ln(C_\infty - C_t)$ against time. C_∞ is the final value of conductivity of a solution and C_t the value of conductivity at time t. All the kinetic data were reproducible to better than ±10%.

Solubilities

The solubilities of the platinum(II) complexes and thiourea in methanol and acetonitrile were determined by equilibrating at 25.0 ± 0.5 °C, up to a reproducible constant concentration. Methanolic solutions of hydrochloric acid (5×10^{-5} mol dm^{-3}) were used for the two complexes; it was proved that this concentration of hydrochloric acid does not affect the solubility of complex(II). The concentration of the saturated solutions was followed by spectrophotometric measurements at two different wavelengths. The solubilities are given in Table I together with transfer chemical potentials of the reactants.

TABLE I. Solubilities (10^{-2} mol dm^{-3}) and Transfer Chemical Potentials, $\delta_m\mu^\ominus$, (kJ mol^{-1}) of Platinum(II) Complexes and Entering Ligands at 25 °C in Methanol and Acetonitrile.

	CH_3OH	CH_3CN	$\delta_m\mu^\ominus$
[Pt(bipy)(ethanolam)Cl]BPh_4*	0.72	0.09	+19.5
[Pt(bipy)(ethylam)Cl]BPh_4*	0.35	1.8	+1.1
[tu]**	132.0	19.0	+4.8
[Br^-]***			+20.5

*The solubilities of the complexes were determined in methanol containing hydrochloric acid (5×10^{-5} mol dm^{-3}). **The solubility of tu refers to the chromatographic commercial product (0.1% water) which was employed for the kinetic experiments. ***From ref. 10.

The thiourea solubility in acetonitrile increases with the presence of traces of water. The solubility and kinetic data reported in this paper refer to a chromatographic commercial product containing 0.1% water.

The accuracy of solubility data was better than 10%.

Transfer Functions

Solubilities and rate parameters provide a basis for the calculation of transfer chemical potentials [3, 6]. These quantities are reported in Table I and II, where the symbol $\delta_m\mu^\ominus$ stands for the transfer chemical potentials of the different compounds studied in the standard state (a concentration of 1 mol dm^{-3}). The summation $\Sigma\delta_m\mu^\ominus(R)$ accounts for the chemical potentials of both reactants in the relative second-order reaction and gives immediately the essential features of the solvent effect on the initial state. The $\delta_m\mu^\ominus$ were calculated assuming that no change in the solid phase in contact with the different solvents takes place [7]. Then $\delta_m\mu^\ominus(A) = RT \ln(S_{MeOH}(A))/(S_{CH_3CN}(A))$ in which $S_{MeOH}(A)$ and $S_{CH_3CN}(A)$ are the solubilities (in mol dm^{-3}) of the reactant A in methanol and acetonitrile, respectively. $\mu^\neq$ refers to the chemical potentials of the transition states; the corresponding transfer functions were calculated from:

$$\delta_m\mu^\neq = \delta_m\mu^\ominus(R) + \delta_m\Delta G^\neq$$

The activation Gibbs function $\delta_m\Delta G^\neq$ follows from $\delta_m\Delta G^\neq = RT \ln(k_{MeOH})/(k_{CH_3CN})$ where k are the second-order rate constants in methanol and acetonitrile, respectively. A diagram which gives the essential features of the solvent on the chemical potentials of IS and TS is reported in Fig. 1.

TABLE II. Transfer Functions (kJ mol^{-1}) from Methanol to Acetonitrile for the Reactions of Platinum(II) Complexes at 25 °C.

	$\delta_m\Delta G^{\neq}$	$\Sigma\delta_m\mu^{\ominus}(R)$*	$\delta_m\mu^{\neq}$
[Pt(bipy)(ethanolam)Cl]BPh_4 + Br^-	−5.4	40	34.6
[Pt(bipy)(ethanolam)Cl]BPh_4 + tu	+0.8	24.3	25.1
[Pt(bipy)(ethylam)Cl]BPh_4 + Br^-	−3.3	21.6	18.3
[Pt(bipy)(ethylam)Cl]BPh_4 + tu	+3.3	5.9	9.2

*$\Sigma\delta_m\mu^{\ominus}(R) = \delta_m\mu^{\ominus}$(complex) + $\delta_m\mu^{\ominus}$(nucleophile).

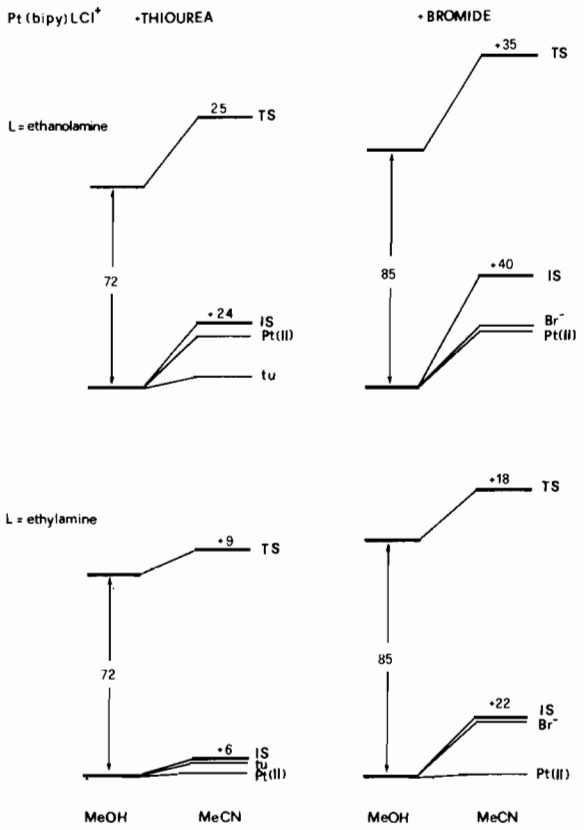


Fig. 1. Variation of chemical potentials, kJ mol^{-1}, of reactants and transition states from methanol to acetonitrile at 25 °C.

Results

Complexes (I) and (II) undergo replacement of the chloride with a variety of nucleophiles. Under pseudo-first order conditions the rate constant relative to these replacements conforms to the usual two terms rate law followed by square planar complexes:

$$k_{obs} = k_1 + k_2[Y]$$

Reactions of [Pt(bipy)(am)Cl]BPh_4, carried out on preparative scale with tetrabutylammonium bromide (TBABr) and thiourea (tu) in the kinetic experimental conditions, led respectively to the isolation of [Pt(bipy)(am)Br]BPh_4 and [Pt(bipy)$(tu)_2$]$(BPh_4)_2$ according to elemental analysis as well as IR spectra of the products. The absorbance changes associated with the reactions of both complexes (I) and (II) with tu clearly indicated that the reactions take place in two distinct kinetic stages: we wanted to decide whether the first or the second refer to the replacement of the amine.

The problem could be solved by means of conductometric experiments; the reactions with tu in fact were associated with well-defined conductivity increases, the initial and the final values being those of 1:1 and 2:1 electrolytes both in methanol and acetonitrile. Not surprisingly, since the conductivity increase stems only from chloride replacement by the neutral tu, in this case the kinetic analysis of the experimental results showed that the formation of the products takes place in only one detectable kinetic stage. The circumstance that there is a close relation between the pseudo-first order rate constants of this stage and those concerning the first stage of the same reactions followed spectrophotometrically indicate that the chloride is the first ligand to be replaced.

The second-order rate constants, with the corresponding conductometric values at zero ionic strength in parentheses, calculated by computer least-squares analysis of the plots of spectrophotometric k_{obs} values against [entering nucleophile] are reported in Table III. In the same table are also reported some of the first-order rate constants, k_1, calculated by an analogous procedure. Owing to the great difference between slopes and intercepts of the plots of k_{obs} against tu, the values of k_1 for this nucleophile proved inaccurate, in the table we only report the k_1 values concerning the TBABr, which could be calculated (especially in methanol) with great accuracy.

Discussion

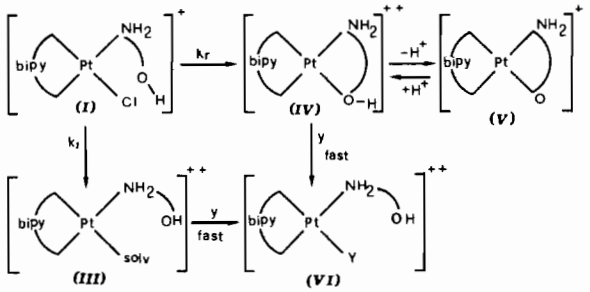
The solubilities of the complexes clearly indicate how much in methanol the presence of the OH in the ethanolamine ligand lowers the chemical potential of complex (I) with respect to complex (II). The reactions rates of the direct replacement from com-

TABLE III. Rate Constants for the Reactions of $[Pt(bipy)(am)Cl]^+$ and tu in Methanol and Acetonitrile at 25 °C. $[Pt(bipy)(am)Cl]^+ + Y \rightarrow [Pt(bipy)(am)Y]^{++} + Cl^-$ (am = ethanolamine and ethylamine, Y = TBABr, tu).

	Y	Solvent	$10^5 k_1$ (s^{-1})	$10^2 k_2$ ($dm^3\ mol^{-1}\ s^{-1}$)
$[Pt(bipy)(ethanolam)Cl]^+$ (I)	TBABr	CH_3OH	73 ± 5	7.0 ± 0.2
	tu			1526 ± 80(1350)
$[Pt(bipy)(ethylam)Cl]^+$ (II)	TBABr	CH_3OH	8.3 ± 3	7.2 ± 0.1
	tu			1289 ± 97(1150)
$[Pt(bipy)(ethanolam)Cl]^+$ (I)	TBABr	CH_3CN	5.6 ± 0.6	6.1 ± 0.3
	tu			110 ± 5(103)
$[Pt(bipy)(ethylam)Cl]^+$ (II)	TBABr	CH_3CN	3.8 ± 0.7	2.7 ± 0.3
	tu			33.7 ± 1.6(33)

plex (I) and (II) show that in such solvent the kinetic behaviour of the two substrates is similar. These findings suggest that in methanol the same kind of interactions with the hydroxylic group lowers both the initial and the transition state of complex (I) to the same extent, leaving the activation energy for the replacement of the chloride unaffected [3, 6].

The only significant difference between the two complexes in methanol concerns the values of k_1. This term is generally taken to refer to a rate determining displacement of the leaving group by a solvent molecule (solvolysis) followed by the fast introduction of the entering nucleophile in place of the solvent molecule. We suggest that, in the case of complex (I), the hydroxylic group supplies through a ring closing process an additional pathway to the solvolysis, as shown in Scheme 1:



Scheme 1

Interestingly in methanol the value of k_1, which could be calculated with small uncertainty only for the reactions of both complexes with TBABr, for the ethanolamine derivative is very close to the first-order rate constant reported for the ring closing process of the same complex in the same solvent [5], and about ten times faster than the solvolytic pathway, k_1, concerning the chloride replacement from the ethylamine derivative. According to the Scheme, basic solutions of complex (I) lead to the quantitative formation of the chelate (V) [5], while the reverse reaction of the chelate in the presence of nucleophile and acid is a very fast reaction, which prevents this species from accumulating [8].

The similarity in methanol between the second-order rate constants, k_2, relative to the direct replacement of the chloride from complexes (I) and (II), is no longer observed when the process takes place in a polar aprotic solvent like acetonitrile (Table I). In this solvent the nucleophilic substitution of the chloride from complex (I) occurs two–three times faster than from complex (II), the activation Gibbs functions, $\delta_m \Delta G^+$, for both nucleophile for the latter complex, being about 2–3 kJ mol^{-1} higher than for complex (I) on going from methanol to acetonitrile. In our opinion this difference can be ascribed to anchimeric assistance provided only in acetonitrile by the ethanolaminic hydroxo residue to the leaving chloride through hydrogen bond interactions. This implies that, in this solvent, an unusually high level of synchronicity in the bond-making and bond-breaking process makes solvation of the leaving group kinetically important [4].

Another remarkable aspect of these reactions is the nucleophilic discrimination which appears to be reduced on going from methanol to acetonitrile for both complexes. A possible interpretation is that only when bond-breaking becomes rate limiting (in the classical reaction profile of two maxima separated by a minimum corresponding to a transient 5-coordinate intermediate) does the breaking of the bond with the entering nucleophile contribute to k_2 [9].

In acetonitrile the bond-breaking maximum should rise with respect to bond-making; therefore in this solvent the donor properties of the ligand could exert opposite effects on the reaction rates leading to the reduced nucleophilic discrimination of the complexes.

In conclusion, our results suggest that the kinetics of chloride replacement from complexes (I) and (II) are largely controlled by the hydrogen-bonding properties of the solvent. The methanol supplies itself OH residues in proximity of the leaving chloride, cancelling out every contribution of the *cis*-coordinated ethanolamine to the nucleophilic replacement. Vice versa, the acetonitrile is much less effective in providing hydrogen-bonding interactions with the leaving chloride which, therefore welcomes the assistance of the ethanolaminic hydroxo residue, which is less shielded than in methanol by solvent interactions.

Supplementary Material Available

A listing of observed rate constants, k_{obs}, as a function of the nucleophile concentration (two Tables) is available upon request.

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References

1 S. Balt and J. Meuldijk, *Inorg. Chim. Acta, 47*, 217 (1981).
2 S. Balt and J. Meuldijk, *Z. Naturforsch., 34b*, 843 (1979).
3 M. J. Blandamer and J. Burgess, *Coord. Chem. Rev., 31*, 93 (1980).
4 L. Cattalini, *Progress in Inorg. Chem., 13*, 263 (1970).
5 E. Rotondo, R. Pietropaolo, V. Marsala and F. Faraone, *J. Inorg. Nucl. Chem., 37*, 1465 (1975).
6 M. J. Blandamer, J. Burgess and J. G. Chambers, *J. Chem. Soc. Dalton Trans.*, 60 (1977).
7 H. Schneider, *Topics in Current Chemistry, 68*, 103 (1976).
8 E. Rotondo, unpublished results.
9 G. Bonivento, L. Canovese, L. Cattalini, G. Marangoni, G. Michelon and M. L. Tobe, *Inorg. Chem., 22*, 802 (1983).
10 B. G. Cox, *Ann. Rep. Chem. Soc., 70A*, 249 (1974).