Effects of Added Alkali-metal and Alkylammonium Bromides on the Kinetics of Reaction Between the $[PdCl\{Et_2N(CH_2)_2NH(CH_2)_2NEt_2\}]^+$ Cation and Bromide Ion in Aqueous Solutions

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Rate constants are reported for the reaction between bromide ions and the complex ion $[PdCl(tedien)]^+$ (tedien = *NNN''N''*-tetraethyldiethylenetriamine) in aqueous solution containing various concentrations of bromide salts. The first-order rate constant for the unimolecular substitution reaction decreases with increase in salt concentration, the effect being more marked through the series $NBu^n_4{}^+ > NPr_4{}^+ > NEt_4{}^+ > NMe_4{}^+ > K^+ \simeq Na^+$. Comparison of rate data and solubilities of the complex chloride salt in 1.0 mol dm^{-3} KCl, $[NEt_4]Cl$, and $[NBu_4]Cl$ indicates that the dominant salt effect operates on the transition state, where hydration and ion-size effects lead to a marked destabilisation.

In aqueous solution, the rate constants of a reaction involving neutral or ionic reactants are extremely sensitive to the concentration and nature of the added salt. Where the reactants are ionic and where there is either a cancellation or generation of charge, the classic Bronsted–Bjerrum theory of salt effects can be used to calculate the dependence of rate constants on ionic strength. However, agreement between theory and experiment is often poor, particularly if the Debye–Hückel limiting law is used to relate ionic activity coefficients of reactants and transition state to the concentration of added salt. Indeed the patterns shown by plots of rate constant against salt concentration are complicated. For example,[1] addition of potassium bromide leads to a decrease but addition of tetra-n-butylammonium bromide leads to an increase in the rate constant for the aquation of the iron complex cation, $[Fe(nphen)_3]^{2+}$ (nphen = 5-nitro-1,10-phenanthroline). We have examined these and related salt effects for various reaction types and solvent systems.[2,3] In addition we have used [4] a statistical thermodynamic calculation in order to probe the roles of solute and ionic hydration, and of ion-size effects. For the most part, however, we have only been able to examine trends in rate constants. Consequently it has not been possible to identify in the case of, for example, an increase in rate constant produced by added salt whether this trend has arisen from a destabilisation of the initial state or stabilisation of the transition state.

Clearly, additional non-kinetic information is required before the analysis can be taken a stage further. This is the approach we have adopted here in an investigation of the effect of added salts on bromide substitution in the $[PdCl(tedien)]^+$ cation (tedien = *NNN''N''*-tetraethyldiethylenetriamine or 3,9-diethyl-3,6,9-triazaundecane) in aqueous media.

In contrast to the majority of square-planar complexes which undergo substitution by parallel first- and second-order processes [5] [equation (1)], substitution at the $[PdCl(tedien)]^+$ cation usually follows the simple first-order rate law of equation (2).[6] The bulky ligand substituents prevent significant associative attack by all but the most powerful nucleophiles at relatively high concentrations; bromide substitution follows the rate law given by equation (2).[7] We have therefore determined first-order rate constants for dissociative substitution in aqueous solutions containing various concentrations of added bromide salts, *e.g.* NaBr, KBr, $[NMe_4]Br$, $[NEt_4]Br$, $[NPr_4]Br$, and $[NBu^n_4]Br$. In addition we have measured the solubility of the complex salt in a range of salt solutions. The salts used here have to be chlorides, to prevent any aquation of the palladium complex.

$$-d[\text{complex}]/dt = \{k_1 + k_2[\text{nucleophile}]\}[\text{complex}] \quad (1)$$

$$-d[PdCl(tedien)^+]/dt = k_1[PdCl(tedien)^+] \quad (2)$$

EXPERIMENTAL

Materials.—These were prepared in the manner described previously.[1,3,7]

Kinetics.—Rate constants were calculated [7] from the change in absorbance at 345 nm for solutions at 298 K containing 1.72×10^{-3} mol dm^{-3} complex (chloride salt).

Solubilities.—The solubilities of the complex (the chloride salt) were measured in a series of solutions containing 1.0 mol dm^{-3} of KCl, $[NEt_4]Cl$, or $[NBu^n_4]Cl$. The saturated solutions were maintained at 298 K for a period of several days and analysed using a Unicam SP1800 spectrophotometer and a Perkin-Elmer 360 atomic absorption spectrometer operating with a single-element palladium lamp.

RESULTS

The first-order rate constants for the substitution reaction between $[PdCl(tedien)]^+$ cations and bromide ions are summarised in Table 1. In all solutions, the change of absorbance with time followed first-order kinetics over more than 2.5 half-lives. Repetitive scans of the absorption spectra showed a gradual change with time and two well defined isosbestic points at 361 and 265 nm. The kinetic data, summarised in the Figure, show that with increase in concentration of added bromide salt the rate constant decreases, the effect being more marked through the series of salts where the order of cation is $NBu^n_4{}^+ > NPr_4{}^+ > NEt_4{}^+ > NMe_4{}^+ > K^+ \simeq Na^+$.

The solubility data obtained from the atomic absorption measurements, summarised in Table 2, show that in a salt solution, concentration 1.0 mol dm^{-3}, the effect on solubility

TABLE 1

Rate constants at 298 K for the reaction between [PdCl(tedien)]$^+$ cations and bromide ions in aqueous solutions containing added salts

Salt	Concentration of salt/ mol dm^{-3}	10^3k/s^{-1}
None	0	2.43
KBr	0.5	2.39
KBr	1.0	2.31
NaBr	0.5	2.41
NaBr	1.0	2.16
[NMe$_4$]Br	0.5	2.06
[NMe$_4$]Br	1.0	1.80
[NEt$_4$]Br	0.5	1.71
[NEt$_4$]Br	1.0	1.38
[NPr$_4$]Br	0.25	1.75
[NPr$_4$]Br	0.5	1.50
[NPr$_4$]Br	1.0	1.03
[NBu$^n_4$]Br	0.2	1.71
[NBu$^n_4$]Br	0.5	0.896
[NBu$^n_4$]Br	1.0	0.712
KI	0.5	2.00
KI	1.0	2.02

TABLE 2

Solubility of [PdCl(tedien)]Cl in three salt solutions, 1.0 mol dm^{-3}, at 298 K

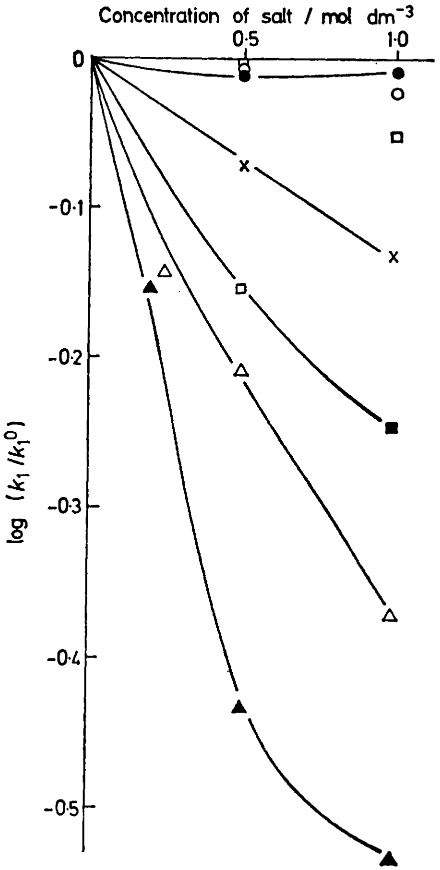
Salt	KCl	[NEt$_4$]Cl	[NBu$^n_4$]Cl
Solubility/mol dm^{-3}	1.04	1.08	1.35

of the complex has the order [NBu$^n_4$]Cl > [NEt$_4$]Cl > KCl. This trend was confirmed by the absorption spectra of the saturated solutions in the visible region.

DISCUSSION

The striking observation is the sensitivity of the rate constant to the concentration of added salt and the nature of the added cation (Figure). The latter observation is perhaps unexpected bearing in mind that the reaction involves first-order unimolecular dissociation of a cation. It is noteworthy that a Bronsted–Bjerrum analysis using the Debye-Hückel limiting law would predict no change in rate constant when a salt is added. A similar point was made in our analysis [1] of the effects of added salts on the rate constant for the aquation of the [Fe(nphen)$_3$]$^{2+}$ cation. As before [1] we could extend this analysis to include the full Debye–Hückel equation for ionic activity coefficients, using different radii for initial and transition states, but in our experience the agreement between theory and experiment is poor. For this reason we have attempted in this work to estimate independently the effect of added salt on the initial state.

In comparing the initial and transition states, it seems reasonable to assume that the transition state is larger than the initial state. This conclusion stems from a consideration of the mechanism of reaction. Thus on activation there is considerable stretching of the Pd–Cl bond and contemporary charge development on the chloride atom, with associated enhancement of Cl–solvent interaction. At the transition state, a balance is struck between neighbouring solvent–solvent interaction and Cl–solvent interaction. Beyond some initial stage of charge development, exothermic solvation of the developing anion increases until the full charge is produced on the chloride ion on the product side of the energy profile for the reaction. Strong solvent–Cl interaction at the transition state implies that the transition state is more hydrophilic (less hydrophobic) than the initial state. Indeed, in view of the character of the tedien ligand, the hydration of the initial state resembles that of an alkylammonium ion where around the ion, solvent–solvent interaction is enhanced relative to that in water at the same temperature and pressure, but solvent–solute interaction is weak.



Effect of added bromide salts on the rate constant for the first-order unimolecular substitution reaction of bromide ions with [PdCl(tedien)]$^+$ at 298 K in aqueous solution; cations are K$^+$ (○), Na$^+$ (□), [NMe$_4$]$^+$ (×), [NEt$_4$]$^+$ (■), [NPr$_4$]$^+$ (△), and [NBu$^n_4$]$^+$ (▲); also included are data for the effect of added potassium iodide (●)

It is therefore interesting to observe that in the Figure, the curves follow an order anticipated if the size of the cation is the determining factor.[3,4] However, the solubility data show that for the initial state, the trend of increasing stabilisation is opposite to that predicted by this line of argument. Here we observe the impact of the second effect, namely the hydration characteristics of the ions involved. In a solution of a salt or mixture of salts where the concentration is as high as 1.0 mol dm^{-3}, the role of hydration effects can be understood in terms of the effects of overlapping solvent co-spheres.[8] These co-spheres define a region of solvent around a solute (neutral or charged) where the structure of the solvent is determined by the solute. In real solutions, these co-spheres overlap and, depending on the perturbation of the solvent in the overlap region, the solutes are stabilised or destabilised. In general terms[8] overlaps of co-spheres formed by solutes having similar hydration characteristics are favourable and lead to a mutual stabilisation of the solutes, *i.e.* a lowering of chemical potential. Where the hydration co-spheres are dissimilar, overlap leads to mutual destabilisation of the solutes. In the present context it follows that in the KBr solutions, overlap of K^+ co-sphere with the positively charged initial state is a destabilising influence but, with the transition state, a stabilising influence. Replacement of K^+ by $[NEt_4]^+$ and then, more significantly, by $[NBu^n{}_4]^+$ leads to a relative stabilisation of the initial state and a destabilisation of the transition state.

If we now consider these two effects, ion size and hydration, together, they result in different effects on the initial state. The results indicate that the hydration effect is more important, leading to a slight increase in solubility. However, the two effects will operate together on the transition state, producing a marked destabilisation. In these terms, the fall in rate constant as salt is added (Figure) appears to be dominated by the effect of added salt on the transition state.

We thank the S.R.C. for a grant (to S. J. H.).

[9/436 *Received*, 16*th March*, 1979]

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