Kinetics and Mechanism of Substitution on Square-planar Palladium(II) Complexes in Mixed Aqueous Solvents

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The kinetics of halide replacement in the complexes [Pd(iea)X]X and [Pd(ieda)X]X [iea = iminobis(ethyleneamine) and ieda = iminobis(ethylenediethylamine); X = Cl^- or I^-] have been measured in a variety of mixed aqueous organic solvents. The rate expression is Rate = $k_1 + k_2[X^-]$. Plots of log k_1 and log k_2 against the Grunwald–Winstein Y values are linear with gradients of between 0.33 and 0.63. The results are interpreted in terms of a similar associative mechanism for each reaction, involving appreciable Pd–X bond cleavage in the rate-determining transition state. The utility of log k against Y plots and other linear free-energy relations (such as rate–equilibrium correlations) in elucidating the intimate mechanisms of square-planar substitutions are discussed.

FOLLOWING the success of mixed-solvent studies in elucidating the mechanisms of organic solvolysis reactions,[1] several reports have recently appeared [1-10] in which this approach has been extended to the reactions of co-ordination complexes. The majority of these reports concerns the aquation of octahedral aminechlorocobalt(III) complexes, for which a linear relation was shown [5,6] to exist between log k and the Grunwald–Winstein Y values. (These Y values appear to be a good qualitative measure of the ionising or solvating ability of the solvent mixture.) The magnitude of the gradient (m 0.23—0.36) was interpreted as suggesting a dissociative S_N1 mechanism for these aquations. Similar m values have recently been obtained for aquation of octahedral aminechlororuthenium(III) complexes,[11] whereas significantly lower gradients have been reported for chromium(III) (m 0.12) [9] and iron(II) complexes (m 0.1—0.2).[4,7] By analogy with the organic solvolysis studies, it has been suggested that the comparatively low gradients for Cr^{III} and Fe^{II} indicate some degree of associative (S_N2) character in their substitution reactions.

In view of the recognised dependence of the Y values (and hence m) on the choice of standard organic substrate,[12] the validity of drawing mechanistic conclusions from mixed-solvent studies with co-ordination complexes as substrates is uncertain. In particular, studies are lacking for model S_N1 and S_N2 inorganic reactions. The absence of any well established S_N2 reaction precludes such a model study with octahedral metal complexes. However, among square-planar complexes, the species $[Pd(iea)Cl]^+$ and $[Pd(ieda)Cl]^+$ [iea = iminobis(ethyleneamine) and ieda = iminobis(ethylenediethylamine)] might be considered to provide such models, since while substitution at the former occurs by the S_N2 path characteristic of Pd^{II} complexes,[13] the sterically hindered $[Pd(ieda)Cl]^+$ is believed [14] to be compelled to react *via* a solvent-assisted dissociative (S_N1) mechanism.

This paper reports and compares the kinetics of iodide substitution on these two Pd^{II} complexes in a variety of mixed-aqueous solvents [equation (1)] and kinetic data for chloride substitution on the corresponding iodo-complexes [equation (2)]. However, while this investigation was in progress a more recent study of the

$$[Pd(L)Cl]^+ + I^- \quad [Pd(L)I]^+ + Cl^- \qquad (1)$$

$$[Pd(L)I]^+ + Cl^- \quad [Pd(L)Cl]^+ + I^- \qquad (2)$$

$[Pd(ieda)X]^+$ (X = Cl, Br, or I) complexes appeared,[15] which indicated that while a dissociative substitution mechanism indeed operates for aprotic solvents such as dimethyl sulphoxide (dmso) and *NN*-dimethylformamide (dmf), substitution in protic solvents (especially water) proceeds by an essentially associative mechanism. The present kinetic results in mixed solvents are therefore discussed in terms of their mechanistic significance for square-planar Pd^{II} complexes.

EXPERIMENTAL

Materials.—The complexes [Pd(ieda)X]X and [Pd(iea)X]X (X = Cl or I) were prepared by published procedures,[14] and their purity checked by chemical analysis and comparison of their u.v.–visible spectra with published data [14] {Found: C, 36.5; H, 7.1; N, 10.8. Calc. for [Pd(ieda)Cl]Cl: C, 36.7; H, 7.4; N, 10.7. Found: C, 16.8; H, 4.5; N, 14.9. Calc. for [Pd(iea)Cl]Cl: C, 17.1; H, 4.7; N, 14.9. Found: C, 24.8; H, 5.3; N, 7.0. Calc. for [Pd(ieda)I]I: C, 25.0; H, 5.1; N, 7.3. Found: C, 10.2; H, 2.8; N, 9.0. Calc. for [Pd(iea)I]I: C, 10.4; H, 2.8; N, 9.1%}. All other reagents and solvents were of analytical purity.

Kinetic Measurements.—(a) The reactions of the [Pd(ieda)X]X (X = Cl or I) complexes were slow enough to follow by conventional techniques. Reagent solutions of the desired composition were prepared, and 2.5 cm^3 carefully pipetted into a 1 cm silica cell thermostatted at the

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[1] (*a*) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846; (*b*) A. H. Fainberg and S. Winstein, *ibid.*, 1956, **78**, 2770; (*c*) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, 1951, **73**, 2700; (*d*) H. D. Cowan, C. L. McCave, and J. C. Warner, *ibid.*, 1950 **72**, 1194; (*e*) C. Reichardt, *Angew. Chem. Internat. Edn.*, 1965, **4**, 29; (*f*) P. R. Wells, *Chem. Rev.*, 1963, **63**, 171.

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[3] V. D. Panasyuk and A. V. Arkharov, *Russ. J. Inorg. Chem.*, 1968, **13**, 1279. and refs. therein.

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[5] J. Burgess, *J. Chem. Soc. (A)*, 1970, 2351, 2703.

[6] J. Burgess and M. G. Price, *J. Chem. Soc. (A)*, 1971, 3108 and refs. therein.

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[9] J. Burgess, *J.C.S. Dalton*, 1973, 825.

[10] (*a*) V. D. Panasyuk and N. F. Malashok, *Russ. J. Inorg. Chem.*, 1969, **14**, 525; (*b*) *ibid.*, p. 661; (*c*) V. D. Panasyuk and T. I. Denisova, *ibid.*, 1970, **15**, 1442.

[11] L. A. P. Kane-Maguire and G. Thomas, *J.C.S. Dalton*, 1975, 1324.

[12] L. Wilputte-Steinert and P. J. C. Fierens, *Bull. Soc. chim. belges*, 1955, **64**, 308.

[13] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, ch. 5.

[14] W. H. Baddley and F. Basolo, *J. Amer. Chem. Soc.*, 1966, **88**, 2944.

[15] R. Roulet and H. B. Gray, *Inorg. Chem.*, 1972, **11**, 2101.

desired temperature (±0.1 °C) in a Beckman DK2A spectrophotometer. After waiting 20 min for temperature equilibrium, an accurately weighed sample (1 mg using a microbalance) of the complex was added. This amount of sample gave solutions containing [Pd^{II}] *ca.* 7 × 10^{-4} and *ca.* 1 × 10^{-3}M, for X = I^- and Cl^-, respectively.[*] The cell was restoppered, shaken to effect solution, and replaced in the thermostatted compartment.

The progress of the reaction of [Pd(ieda)Cl]Cl with 0.1M-NaI [equation (1)] was then followed by observing the decrease in absorbance of the starting material peak at 346 nm. On the other hand, the growth of this peak was followed for the corresponding reaction of [Pd(ieda)I]I with 0.1M-NaCl [equation (2)]. Pseudo-first-order rate constants were obtained from gradients of plots of log ($A_\infty - A_t$) against time. In the former reaction A_∞ was determined experimentally, while in the latter A_∞ was more conveniently calculated employing the known absorption coefficient of $[Pd(ieda)Cl]^+$ at 346 nm.[14]

(b) Unlike the sterically hindered amine complexes, the reactions of [Pd(iea)X]X (X = Cl or I) were too fast to follow by conventional methods. Instead a thermostatted stopped-flow spectrophotometer similar to that described recently by Michael *et al.*[16] was employed. This design eliminates the thermostatting problems common to other designs by employing a glass-enclosed assembly of quartz light guides–observation port–mixer. A strong visible-light source was provided by using a Bosch and Lomb high-intensity monochromator fitted with variable slits.

For reaction (1) a solution of [Pd(iea)Cl]Cl (3.2 × 10^{-1}M) in pure methanol was placed in one reaction syringe. In this solvent the complex appears stable idefinitely. Appropriate methanol–water solutions of NaI (0.02M, seven-fold excess) were introduced into the other syringe, such that after mixing with the complex solution final solvent compositions of 50, 60, and 70% methanol (v/v) were achieved (and $[I^-]$ = 0.01M). The reaction was followed at 387 nm, an absorption maximum of the iodo-complex product. Reaction traces were recorded and photographed on a Tektronix 564B storage oscilloscope fitted with a log converter, thus affording a direct record of absorbance changes with time. Pseudo-first-order rate constants were determined from gradients of plots of log ($A_\infty - A_t$) against time, the absorbances being assigned arbitrary units.

A similar procedure and solvent range was employed for reaction (2), except that solubility problems required the use of a less concentrated original complex solution ([Pd^{II}] = 1.7 × 10^{-3}M) in methanol. Also the final chloride concentration was varied between 0.1 and 0.5M. Final ionic strength was maintained constant at 0.5M in all cases by the addition of appropriate amounts of sodium perchlorate to the original NaCl solutions. The reaction was monitored by following the disappearance of the initial iodo-complex peak at 387 nm.

The low solubilities of [Pd(iea)X]X (X = Cl or I) in pure ethanol and acetone prevented meaningful stopped-flow kinetic data being obtained in these co-solvents.

RESULTS

For the reaction of [Pd(ieda)Cl]Cl with 0.1M-NaI, good first-order kinetics were obtained for at least 85% completion of reaction in each of the solvent mixtures employed. Kinetic data at 30 °C in water–methanol, –ethanol, and –acetone solvents are collected in Table 1. Most of the rate constants are the average of duplicate determinations, with a reproducibility better than ±3%. Plots of log ($A_\infty - A_t$) against time were linear for at least 70% completion for the corresponding reaction of the complex [Pd(ieda)I]I with 0.1M-NaCl in water–methanol. The rate constants (at 40.0 °C) in Table 2 are again the average of duplicate determinations (reproducibility ±5%).

TABLE 1

Kinetic data for the reaction of [Pd(ieda)Cl]Cl with 0.1M-NaI in mixed aqueous solvents at 30 °C

Organic component (% v/v)	Methanol		Ethanol		Acetone	
	Y	$10^3k/s^{-1}$	Y	$10^3k/s^{-1}$	Y	$10^3k/s^{-1}$
0	3.49	3.23	3.49	3.23	3.49	3.23
10	3.28	2.63	3.31	2.80	3.23	2.17
20	3.03	2.05	3.05	1.69	2.91	1.71
30	2.75	1.54	2.72	1.40	2.48	1.05
40	2.39	1.09	2.20	0.904	1.98	0.640
50	1.97	0.75	1.655	0.557	1.40	0.386

Stopped-flow kinetic data for the reaction of [Pd(iea)Cl]Cl with 0.01M-NaI in water–methanol at 5.5 °C are summarised in Table 3. The rapidity of this reaction contributed to poor reproducibility and prevented kinetic studies at higher iodide concentrations. However, the slower reaction of [Pd(iea)I]I with NaCl could be followed by stopped-flow techniques over a range of chloride concentrations ($[Cl^-]$ = 0.1—0.5M) in aqueous methanol. Plots of log ($A_\infty - A_t$) were generally linear for at least two half-lives. Each of the $k_{obs.}$ values in Table 4 for this latter process at 3.3 °C are the

TABLE 2

Kinetic data for the reaction of [Pd(ieda)I]I with 0.1M-NaCl in water–methanol solutions at 40.0 °C

Methanol (% v/v)	Y	$10^4k/s^{-1}$
0	3.49	7.95
10	3.28	6.32
20	3.03	5.01
30	2.75	3.71
40	2.39	2.67
50	1.97	1.81

TABLE 3

Kinetic data for the reaction of [Pd(iea)Cl]Cl with 0.01M-NaI in water–methanol solutions at 5.5 °C

Methanol (% v/v)	Y	$k_{obs.}$[*]$/s^{-1}$
50	1.97	25.6
60	1.49	13.8
70	0.96	9.2

[*] Average of quadruplicate determinations (reproducibility varied from ±5 to ±15%).

TABLE 4

Kinetic data for the reaction of [Pd(iea)I]I with NaCl in water–methanol solutions at 3.3 °C and I = 0.5M

Methanol (% v/v)	Y	$[Cl^-]$/M	$k_{obs.}/s^{-1}$	k_1/s^{-1}	$k_2/l\ mol^{-1}\ s^{-1}$
50	1.97	0.20	2.84	1.50	6.70
		0.25	3.16		6.64
		0.35	3.74		6.40
		0.50	4.82		6.64
60	1.49	0.10	1.21	0.99	3.20
		0.25	1.87		3.52
		0.50	2.35		2.72
70	0.96	0.10	0.858	0.70	1.58
		0.25	1.12		1.68
		0.50	1.40		1.40

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[*] 1M = 1 mol dm^{-3}.

[16] D. Michael, D. O'Donnell, and N. H. Rees, *Rev. Sci. Instr.*, 1974, **45**, 256.

average of triplicate determinations (reproducibility ±7%). From plots of $k_{obs.}$ against $[Cl^-]$ in fixed solvent mixtures, the k_1 and k_2 terms in the rate expression (3) could be separated. The second-order nucleophile-dependent rate constants, k_2, in Table 4 were calculated using equation (4).

$$\text{Rate} = k_1 + k_2[Cl^-] \qquad (3)$$

$$k_2 = (k_{obs.} - k_1)/[Cl^-] \qquad (4)$$

The m values collected in Table 5 were obtained from gradients of plots of log k against Y (*e.g.* Figures 1 and 2).

TABLE 5

Summary of m values for reaction of $[Pd(L)X]^+$ complexes with halide ions in mixed water–methanol solvents

	m		
Complex	k_1	k_2	$k_{obs.}$[a]
$[Pd(iea)I]^+$	0.33	0.63	0.45[b]
$[Pd(ieda)I]^+$	0.42		
$[Pd(iea)Cl]^+$			0.44[c]
$[Pd(ieda)Cl]^+$	0.42, 0.43,[d] 0.45[e]		

[a] Combines both k_1 and k_2[Nucleophile] terms. [b] $[Cl^-]$ = 0.25M. [c] $[I^-]$ = 0.01M. [d] Aqueous ethanol. [e] Aqueous acetone.

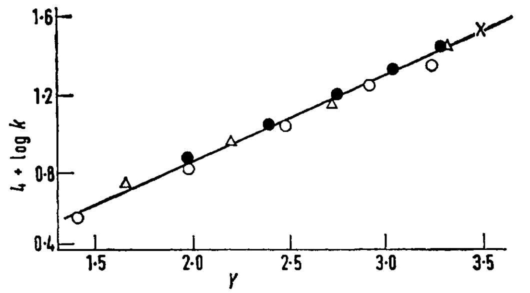


FIGURE 1 Variation of log k_1 with Y for the reaction of $[Pd(ieda)Cl]^+$ with 0.1M-NaI in mixed aqueous solvents: (●), MeOH; (○), Me_2CO; (△), EtOH

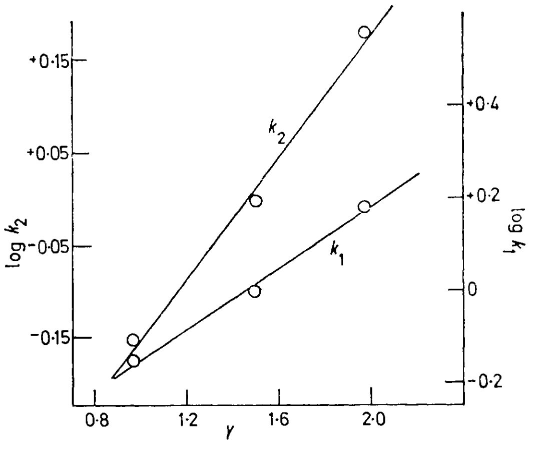


FIGURE 2 Variation of log k_1 and log k_2 with Y for the reactions of $[Pd(iea)I]I$ with NaCl in water–methanol solutions

DISCUSSION

The two-term rate equation (3) previously observed for nucleophilic substitution of $[Pd(iea)X]^+$ type complexes in water indicated the presence of two reaction paths [(5) and (6); L = iea].[13] There is considerable evidence to show that both k_1 (the solvent path) and k_2 (the direct nucleophilic attack route) are essentially associative in character. The present data (Table 4) for the

$$\begin{tikzcd}[Pd(L)X]^+ + H_2O \arrow[r, "k_1", "slow"'] & [Pd(L)(OH_2)]^{2+} + X^- \arrow[d, "Y^-", "fast"'] \\ & [Pd(L)Y]^+ \end{tikzcd} \qquad (5)$$

$$[Pd(L)X]^+ + Y^- \xrightarrow{k_2} [Pd(L)Y]^+ + X^- \qquad (6)$$

reaction of chloride ion on $[Pd(iea)I]^+$ in water–methanol reveal a similar two-term rate equation. At the chloride concentrations employed ($[Cl^-]$ = 0.1—0.5M) the k_1 and k_2 terms make comparable contributions to the observed rate constant. Although no detailed study of the nucleophile dependence for the analogous reaction of iodide ion on $[Pd(iea)Cl]^+$ was possible, the $k_{obs.}$ values obtained probably contain significant contribution from both the k_1 and k_2 paths.

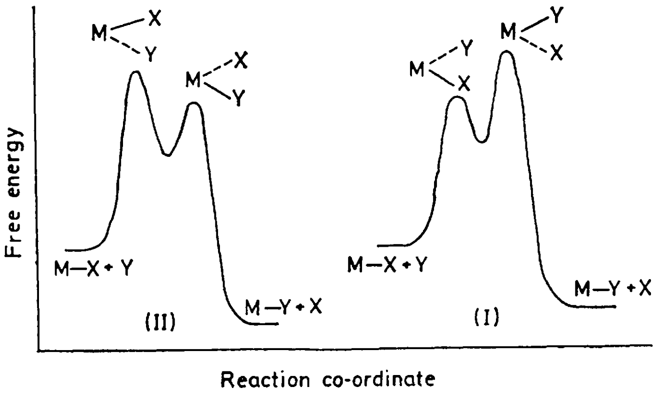
On the other hand, substitution by most nucleophiles in the sterically hindered complexes $[Pd(ieda)X]^+$ is known[14] to proceed entirely *via* the solvent path k_1. Thus the kinetic data reported here for the reactions of $[Pd(ieda)X]^+$ (X = Cl or I; Tables 1 and 2) refer to aquation of these species. At the higher organic-solvent compositions employed the possibility of solvolysis by the methanol or ethanol components could not be eliminated from spectral evidence. However, even at 50% organic component the water is never in less than 2M excess, and since it is known[14] to be about two orders of magnitude more reactive than methanol or ethanol in solvolysis of $[Pd(ieda)X]^+$ substrates nucleophilic interference from the organic component seems very unlikely.

Plots of log k_1 or log k_2 against solvent Y values revealed good correlations for each of the reactions and all solvent mixtures employed (*e.g.* Figures 1 and 2). The scope of the correlation is particularly striking in the case of iodide attack on $[Pd(ieda)Cl]^+$ in water–ethanol mixtures (Figure 1), where a data point for pure ethanol ($k_1 = 1.75 \times 10^{-5}$ s^{-1})[15] fits the log k_1 against Y plot when Fainberg and Winstein's[1b] Y value of -2.033 is employed. Moreover, for this latter reaction almost identical m values are obtained in water–methanol, -ethanol, and -acetone mixtures (0.42, 0.43, and 0.45, respectively; Table 5). These results strongly suggest that linear free-energy relations of the Grunwald–Winstein[1a] type may be successfully applied to square-planar Pd^{II} complexes.

The data in Table 5 show m values in the range 0.33—0.63. Particularly interesting is the comparison between the m values for aquation (k_1) of the unstrained complex $[Pd(iea)I]^+$ and its ieda analogue. Their similar m values in water–methanol (0.33 and 0.42, respectively) indicate that similar solvation requirements are involved in both reactions, suggesting a similarity in mechanism. Such an observation is consistent with the recent n.m.r. and kinetic evidence of Roulet and Gray[15] indicating an essentially associative aquation mechanism for [Pd(ieda)-

X]$^+$ (X = Cl, Br, or I) complexes, like most Pd^{II} substitution processes. However, the magnitude of the slope (*ca.* 0.4) indicates that an S_N2 (lim) process cannot be operating, and that cleavage and solvation of the X$^-$ group must be important in the transition state. Thus, the present mixed-solvent studies suggest the reaction profile (I) during aquation of both [Pd(iea)I]$^+$ and [Pd(ieda)I]$^+$. On the above basis, the high *m* value (0.63) obtained here for direct attack (k_2) of chloride ions on [Pd(iea)I]$^+$ also suggests path (I). In view of the general difficulty [17] in square-planar mechanistic studies of distinguishing between reaction profile (I) and an alternative extreme situation (II) in which metal–nucleophile bond formation is the major feature of the transition state, it appears that mixed-solvent studies may prove a very useful tool in elucidating the intimate mechanism.

Interesting comparison can also be made with recent mixed-solvent kinetic studies[10a,b] on the aquation (k_1) of *cis*-[Pt(NH$_3$)$_2$Cl$_2$], *cis*-[Pt(en)Cl$_2$] (en = ethylenediamine), and *trans*-[Pt(NH$_3$)$_2$Cl$_2$], and for the reaction (k_2) of the last mentioned complex with ammonia. On the basis of rate correlations with solvent dielectric constant, the authors assigned an S_N1 mechanism to the aquations, in contrast to an S_N2 path for the ammonia (k_2) reaction.[10b] Recalculation of the data in terms of solvent *Y* values gives the *m* values in Table 6. As with our Pd^{II} reactions, *m* values are generally in the range 0.33—0.60, except for the low value for the ammonia reaction (*m* 0.14). However, a more attractive interpretation of these results might be that, while the aquations proceed *via* profile (I), the ammonia (k_2) reaction involves path (II).



Comparison with Mixed-solvent Studies on Octahedral Complexes.—The *m* values (Table 5) observed here for square-planar Pd^{II} complexes are significantly higher than those known for aquation of octahedral Co^{III} complexes (*m ca.* 0.3), and very much greater than those reported for similar Cr^{III} complexes. However, in view of the known S_N1 character of the reactions of Co^{III} complexes, and the overall associative nature of Pd^{II} substitutions, it seems unlikely that the higher *m* values found here reflect a greater degree of M–X bond breaking in the transition state of Pd compared to Co complexes. Rather, it would seem to emphasise the dangers involved in attempting comparisons between the solvation properties of octahedral and square-planar complexes. There is considerable evidence to indicate that, apart from normal or general solvation, square-planar complexes are characterised by specific solvation. This arises since they are co-ordinatively unsaturated and can accommodate weak co-ordination of solvent molecules in the axial positions. An adduct of this type, namely [Pt(NH$_3$)$_4$(NCMe)$_2$]Cl$_2$, has been isolated and its structure confirmed by *X*-ray crystallography.[18] Circular dichroism [19] and other spectroscopic [20] and kinetic studies [21,22] support similar solvation of Pt^{II} and Pd^{II} halogeno-complexes. It is possible that specific solvation of the [Pd(iea)X]$^+$ complexes may alter as the solvent mixture changes. If these solvent molecules are lost during formation of the transition state this may influence the magnitude of the observed *m* values.

TABLE 6

Summary of *m* values calculated for the reactions of Pt^{II} complexes in mixed aqueous solvents at 25—30 °C

Complex	Nucleophile	Organic component	*m*
cis-[Pt(NH$_3$)$_2$Cl$_2$] [a]	H$_2$O	MeOH	0.53
		EtOH	0.34
		Me$_2$CO	0.34
cis-[Pt(en)Cl$_2$] [a]	H$_2$O	MeOH	0.60
		EtOH	0.44
		Me$_2$CO	0.33
trans-[Pt(NH$_3$)$_2$Cl$_2$]	H$_2$O	MeOH	0.35
		EtOH	0.39
		Me$_2$CO	0.36
	NH$_3$	MeOH	0.14
		EtOH	0.14
		Me$_2$CO	0.14

[a] Rate constants from ref. 10*a*. [b] Rate constants from ref. 10*b*.

Another possible source of the higher *m* values for Pd^{II} compared to Co^{III} complexes lies in the nature of the M–X bonds. Langford [23] suggested that the low *m* values found for chlorocobalt(III) aquations (compared to t-butyl chloride) may arise partly from the fact that the Co–Cl bond is essentially 'ionic' in the ground-state substrate complex and thus does not require much more ionisation to reach the transition state. Such considerations would not be expected to apply to the halogeno-complexes of the soft Pd^{II} metal ion in which the Pd–X bonds are largely covalent.[24]

A final interesting feature of the *m* values in Table 5 is the essentially identical magnitudes observed for analogous chloro- and iodo-complexes. This result contrasts

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[17] L. Cattalini, 'Mechanisms of Square Planar Substitution,' *MTP Internat. Rev. Sci., Inorg. Chem.*, vol. 9, Butterworths, 1972, p. 269.

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[21] P. Haake and R. M. Pfeiffer, *J. Amer. Chem. Soc.*, 1970, **92**, 5243.

[22] D. G. Cooper and J. Powell, *J. Amer. Chem. Soc.*, 1973, **95**, 1102.

[23] C. H. Langford, *Canad. J. Chem.*, 1971, **49**, 1497.

[24] Ref. 13, ch. 2.

with earlier studies on $\mathrm{Co^{III}}$ systems for which it was observed that bromo-complexes gave significantly lower values (m 0.15—0.25) than corresponding chloro-complexes.[6] Similarly, in organic chemistry t-butyl bromide has m 0.92 compared with m 1.00 for t-butyl chloride.[17]

TABLE 7

Rate constants and calculated equilibria data at 25 °C for the reaction system

$$[\mathrm{Pd(ieda)X}]^+ + \mathrm{H_2O} \underset{k_{\mathrm{an}}}{\overset{k_{\mathrm{H_2O}}}{\rightleftharpoons}} [\mathrm{Pd(ieda)(OH_2)}]^{2+} + \mathrm{X}^-$$

X	$10^3k_{\mathrm{H_2O}}$ [a]/s^{-1}	k_{an} [b]/l mol^{-1} s^{-1}	$K_{\mathrm{an}} = k_{\mathrm{an}}/k_{\mathrm{H_2O}}$
Cl	2.02	7.36	3 640
Br	1.24	5.95	4 800
I	0.30	4.46	14 900

[a] Ref. 15. [b] J. B. Goddard and F. Basolo, *Inorg. Chem.*, 1968, **7**, 936.

Rate–Equilibria Correlations for Aquation of [Pd(ieda)-X]X *Complexes.*—Gradient plots of log $k_{\mathrm{H_2O}}$ against $-\log K_{\mathrm{an}}$ (where K_{an} is the equilibrium constant for anation) have been used by Langford [25] and others as a measure of the degree of leaving-group dissociation in the aquation of octahedral $\mathrm{Co^{III}}$ [25,26] and $\mathrm{Cr^{III}}$ [27] complexes, *e.g.* $[\mathrm{Co(NH_3)_5X}]^{2+}$ ($\mathrm{X = F^-, Cl^-, Br^-, I^-, NO_3^-}$, or $\mathrm{NCS^-}$). However, to date such rate–equilibria correlations have not been extended to the aquation of square-planar systems, although Tobe has recently reported [28] such data for substitutions in some $\mathrm{Pt^{II}}$ complexes. In Table 7 are collected aquation [15] and anation rate constants for $[\mathrm{Pd(ieda)X}]^+$ (X = Cl, Br, or I) complexes at 25 °C. A plot of log $k_{\mathrm{H_2O}}$ against $-\log K_{\mathrm{an}}$ (Figure 3) gives a good correlation with gradient $\alpha \geqslant 1$. Following Langford,[25] one is therefore led to conclude that while the aquations of $[\mathrm{Pd(ieda)X}]^+$ are essentially associative,[15] they proceed *via* reaction profile (I) in which cleavage of the Pd–X bond is important in the rate-determining transition state. This conclusion is the same as that arrived at above on the basis of mixed-solvent m values.

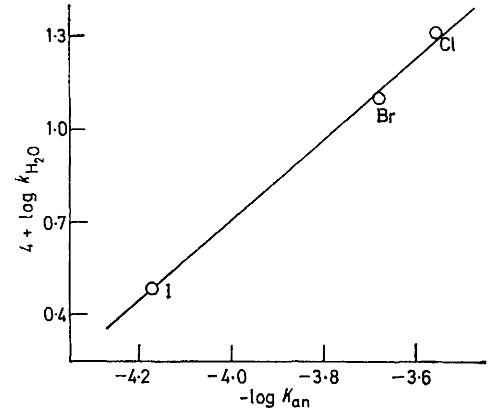

FIGURE 3 Plot of log $k_{\mathrm{H_2O}}$ against $-\log K_{\mathrm{an}}$ for aquation of $[\mathrm{Pd(ieda)X}]^+$ complexes at 25 °C

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