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Solvent Effects in Square Planar Complexes: Kinetics of Substitution at 1-(2-hydroxyphenyl)-3,5-(diphenylformazanato)-platinum(II) Complexes

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A kinetic study at 25 °C is reported of the substitution reaction FoPtX + Y → FoPtY + X (H_2Fo = 1-(2-hydroxyphenyl)-3,5-diphenylformazan), with X = NH_3 and pyridine and Y = thiourea, triphenylphosphine, and the thiocyanate ion, in seven non-aqueous pure solvents The main reaction route is the direct associative displacement of X by Y The mutual dependence of reactivity effects of entering and leaving ligands and solvent was interpreted as indicating a synchronous mechanism Steric effects were also found to be important, probably due to the rigidity of the substrate Solvent effects on the rates are comparatively small With the help of transfer functions from measured solubilities a dissection of solvent effects on initial and transition states was accomplished, for one reaction also the final state could be included in the comparison On the whole non-specific solvation effects dominate and the transfer Gibbs free energy of solvation does not change on going to the transition state Exceptions to this rule are caused by initial state stabilization of two of the entering ligands in the protic solvent methanol and by transition state labilization for $FoPtNH_3$ in strong donor solvents as DMSO and DMF The mechanism for the latter labilization is suggested to be charge transfer to Pt^{2+} caused by solvent donor interaction with coordinated ammonia or directly to the metal centre A similar electronic effect seems to govern the solvent dependence of the ^{195}Pt NMR chemical shift for $FoPtNH_3$

Introduction

Substitution reactions at square planar complexes of d^8 transition metal ions still present a number of complex problems, among which the kinetic role of the solvent [1] and the intimate mechanism [2] In a previous paper [3] we have shown that the study of substitution reactions of metal complexes of 1-(2-hydroxyphenyl)-3,5-diphenylformazan (H_2Fo)

$$\mathrm{FoMX} + \mathrm{Y} \rightarrow \mathrm{FoMY} + \mathrm{X} \qquad (1)$$

presents a comparatively simple system due to the rigidity of the substrate In addition its solubility in a considerable number of non-aqueous solvents of diverging donor and acceptor properties broadens the choice of suitable solvents In this way we tried to attack the problem [4] of the role of solvent in simple electrophile–nucleophile combination reactions for square planar complexes in the much discussed [5] area of distinguishing between specific and general solvational effects Specific effects for the present case will refer to coordination at the vacant axial positions at the metal centre and to interactions between solvent acceptor sites and ligand donor atoms

The published [3] results on the palladium(II) complexes of eqn (1), studied in a limited number of pure solvents, were interpreted as indicating a dominance of non-specific solvation effects in these complexes In addition an unusually high degree of synchronicity of bond-breaking and bond-making in the transition state was suggested Solvents with either strong donor (as dimethylsulphoxide) or strong acceptor (methanol) properties induced exceptional behaviour As discussed, these conclusions demanded a comparison with the analogous platinum(II) systems and an extension of the number of solvents studied After the platinum(II) compounds were available in a pure state [6] the lacking results could be obtained and are presented here in the form of a kinetic study of reaction (1) with M = Pt and X = NH_3, py(ridine), Y = tpp(triphenylphosphine), tu (thiourea) and the thiocyanate ion, in seven pure solvents

Experimental

Chemicals

The preparation of the platinum(II) complexes has been described [6] The remaining chemicals and

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TABLE I. Solubilities S (in units mol dm^{-3})^a of Platinum(II) Formazan Complexes and Ligands Used, at 25.0 °C.

Compound	Solvents						
	Pc	MeOH	An	Ac	DMSO	DMF	Diox
FoPtNH$_3$	−3.68	−5.78	−5.08	−2.79	−1.71	−0.50	−1.57
FoPtpy	−7.09	−9.94	−8.33	−6.83	−5.27	−4.48	−5.97
FoPttpp	−4.12	−6.72	−5.34	−3.45	−3.80	−3.12	−3.07
tu	−0.65	0.28^b	−1.44	−0.67^b	1.39^b	1.39	–
tpp	−1.21	−2.45^b	−1.14^b	0.40^b	−0.37^b	0.50	0.81^b
NH$_3$	−0.22	2.02	0.03	−0.58	0.29	0.11	−0.94

^{a}The entries are lnS. ^{b}From reference [3].

TABLE II. Rate Parameter k$_2$ (in 10^{-6} mol^{-1} dm^3 s^{-1}) and Transfer Functions (in kJ mol^{-1}) for the Direct Displacement Reaction between FoPtX and Y, at 25.0 °C.^{a}

X; Y	Solvents						
	Pc	MeOH	An	Ac	DMSO	DMF	Diox
NH$_3$; tu	197(6)	22(1)	251(5)	175(3)	4.2(3)	15.0(1)	
	0	2.90	5.43	−2.16	−9.94	−12.94	
	0	8.33	4.83	−1.86	−0.40	−6.56	
NH$_3$; tpp	294(2)	399(7)	143(1)	185(2)	19.9(5)	28(2)	159(4)
	0	8.28	3.30	−6.20	−6.97	−12.12	−10.24
	0	7.52	5.08	−5.05	−0.29	−6.29	−8.71
NH$_3$; SCN$^-$	5.1(2)	1.61(2)	5.6(3)	2.94(6)	0.16(4)	0.93(8)	
	0	1.9	6.8	−1.2	−5.7	−0.8	
	0	4.8	6.6	0.2	2.9	3.4	
py; tu	534(3)	89(2)	442(7)	778(2)	174(2)	286(6)	
	0	4.76	5.03	−0.59	−9.57	−11.53	
	0	9.20	5.50	−1.53	−6.79	−9.98	
py; tpp	174(1)	272(6)	277(5)	165(2)	78(2)	61(1)	185(2)
	0	10.14	2.90	−4.64	−6.59	−10.71	−7.78
	0	9.03	1.75	−4.50	−4.60	−8.11	−7.94
py; SCN$^-$	15.2(4)	2.6(2)	12.1(1)	9.0(4)	10.4(3)	14.5(2)	
	0	3.8	6.4	0.4	−5.3	0.6	
	0	8.2	7.0	1.7	−4.4	0.7	

^{a}For each combination of X, Y and solvent the entries are

$$\begin{cases} k_2 \\ \delta_m\mu_{is}^{\ominus} = \Sigma\delta_m\mu^{\ominus}(R) \\ \delta_m\mu^{\neq} \end{cases}$$

The standard deviation is given in parentheses in terms of the last figure of the rate constant.

solvents were purchased in reagent grade and purified if necessary using conventional procedures [3, 7].

Kinetics

Kinetic runs were performed at 25.0 ± 0.1 °C. The slowness of the reactions made it possible to apply conventional spectrophotometry for monitoring, using 1 cm glass cells in a Beckman Acta CIII Spectrophotometer equipped with an automatic timer. The concentration of the platinum(II) complexes was *circa* 10^{-4} mol dm^{-3}; the concentration of the entering ligand was chosen so high in excess that the reverse reaction could be neglected and pseudo first-order conditions were established. Only for the

TABLE III. Kinetic Parameters[a] k_3 (in 10^{-5} mol^{-2} dm^6 s^{-1}) and K (in mol^{-1} dm^3) for the Reaction between FoPtX and Y at 25.0 °C.

X; Y	Solvent					
	Pc	An	Ac	DMSO	DMF	Diox
NH_3; tu	2.1(K)	2.7(K)	1.5(K)	0.15(k_3)		
NH_3; tpp					1.0(k_3)	5.3(k_3)
py; tu	1.0(K)		1.0(K)			
py; SCN^-			5.5(k_3)			

[a] Accuracy 10%.

reaction with the ionic thiocyanate a constant ionic strength of 0.10 mol dm^{-3} (added sodium perchlorate) was employed, to eliminate the effect of changes in ion-association on varying the thiocyanate concentration. The reactions were monitored in the region of maximal spectral change: 18,000 to 23,000 cm^{-1}, and were wavelength independent in that region. The reactions were followed up to 90% completion, with the exception of the relatively slow reactions with SCN^-, where for FoPtpy 50–70% and for FoPtNH$_3$ 10% completion was reached. In the latter cases the absorbance of the final product was determined by raising the temperature. The rates were measured in the following solvents: propylene carbonate (Pc), methanol (MeOH), acetonitrile (An), acetone (Ac), dimethylsulphoxide (DMSO), dimethylformamide (DMF) and 1,4-dioxane (Diox). For solubility reasons only tpp could be used as entering ligand in Diox.

Solubilities

The solubilities of the platinum complexes and the incoming ligands were determined as described [3]. The solubility of ammonia gas was determined at 25.0 ± 0.1 °C and atmospheric pressure by saturating the various solvents with ammonia, distilled from potassium. The concentration of ammonia followed from a conductometric titration. All solubility data are averages from at least two independent determinations. The accuracy is generally better than 2%. The results are in Table I.

NMR Spectra

The ^{195}Pt{^{1}H} NMR spectra were recorded on a Bruker WH-90 multinuclear NMR Spectrometer, operating at 19.32 MHz, using 10 mm tubes. The chemical shifts were calculated relative to the ^{195}Pt signal in the solvent propylene carbonate.

Results

Reactions (1) were followed in the various solvents under pseudo first-order conditions, realized by a sufficiently high concentration of the entering ligand, [Y]. The dependence of the measured rate on [Y] was studied by varying [Y] over one order of magnitude (generally 8 concentrations) [8]. The majority of the systems was found to obey the usual two-term rate-law for square-planar substitution [9, 10]:

$$k(\mathrm{obsd}) = k_1 + k_2[Y] \qquad (2)$$

Where k(obsd) is the observed pseudo first-order rate-constant. A computerized least-squares procedure generally gave fits better than 1%.

A limited number of systems – denoted as (X, Y, solvent) – did not follow equation (2) within the 1% error limit, but did so for an extended version of the equation. So the rate constant for the systems (py, SCN^-, Ac), (NH_3, tpp; DMF and Diox), and (NH_3, tu, DMSO) obeyed equation (3):

$$k(\mathrm{obsd}) = k_1 + k_2[Y] + k_3[Y]^2 \qquad (3)$$

The systems (py, tu; Pc and Ac) and (NH_3, tu; Pc, An and Ac) followed equation (4):

$$k(\mathrm{obsd}) = k_1 + \frac{k_2[Y]}{1 + K[Y]} \qquad (4)$$

The regression parameters resulting from the least-squares fitting are in Table II and Table III. From these it will be seen that the main reaction route is given by k_2, exemplifying the direct displacement of X by Y in eqn. (1). The other terms are small corrections. Of these k_1 stands for a rate-determining solvolysis path, followed by a rapid substitution of the solvent by the entering group (negligible in many of the present systems, which is not unusual for platinum(II) [9, 10]). The small quadratic term (k_3) may indicate an attack of the entering group on a substrate + entering-group associate. Formation of a non-negligible amount of associate will result in a saturation term (K). The erratic appearance of the k_3 and K terms makes them rather useless for mechanistic inferences. We will therefore focus on the k_2

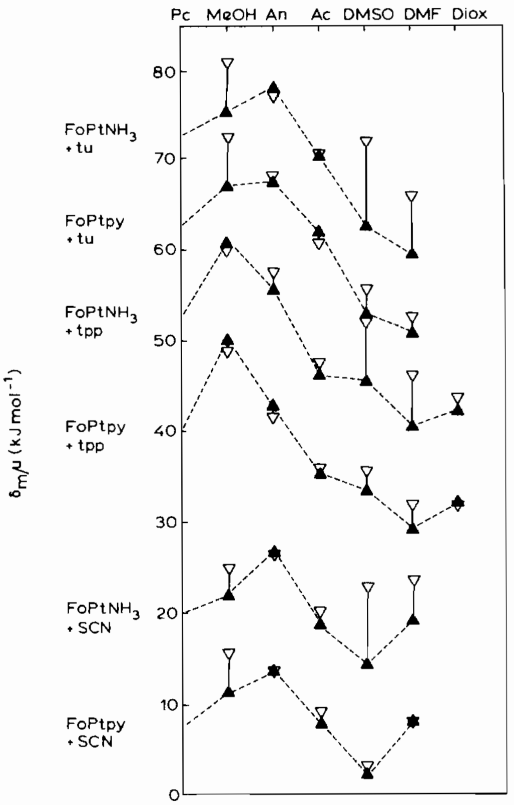

Fig. 1. Variation of transfer chemical potential of reactants (▲) and transition state (▽) for the reactions between FoPtX and Y, with propylene carbonate as reference solvent, at 25.0 °C. The reference potential (μ = 0) is vertically displaced. Values of corresponding states are connected.

term. In view of the appearance of a saturation term (1 + K[Y]) in a few cases, k_2 might be a composite quantity. No further splitting of k_2 was attempted, as there is no reliable basis on which this can be done.

Transfer Functions

Transfer functions were used to effect a dissection of initial and transition state solvent effects [11, 12]. For the platinum(II) complexes and the entering and leaving ligands transfer chemical potentials $\delta_m\mu^{\ominus}$ were calculated from the measured solubilities, based on the usual assumptions [12], with the exception of the thiocyanate ion, for which literature values [13, 14] were used, as explained before [3]. The transfer chemical potential for the transition state $\delta_m\mu^{\neq}$ follows from those of the reactants and the Gibbs free energy of activation $\Delta G^{\neq}$:

$$\delta_m\mu^{\neq} = \sum_{\text{reactants R}}\delta_m\mu^{\ominus}(R) + \delta_m\Delta G^{\neq} \qquad (5)$$

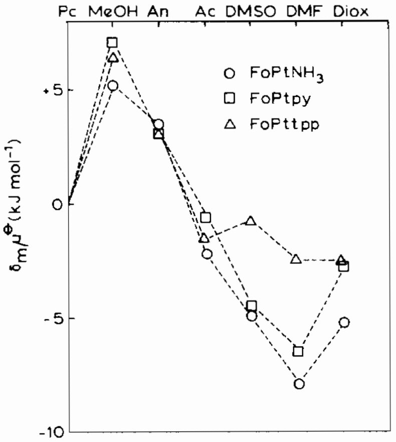

Fig. 2. Variation of transfer chemical potential with solvent for the platinum(II) formazan complexes. Values at 25.0 °C. Reference solvent propylene carbonate.

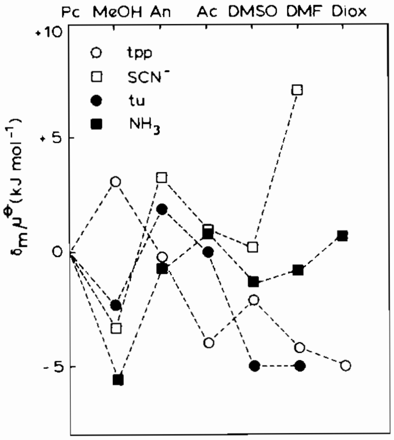

Fig. 3. Variation of transfer chemical potential of ligands with solvent. Values at 25.0 °C. Reference solvent propylene carbonate.

$$\delta_m\Delta G^{\neq} = RT \ln \frac{k_{RS}}{k_S} \qquad (6)$$

where k is the rate constant, measured in the reference solvent: k_{RS} and the other solvents: k_S.

Propylene carbonate was chosen as the reference solvent, as this solvent seems to meet a number of requirements for this [15].

Transfer chemical potentials of reactants and transition state for the k_2 reaction are displayed in Fig. 1. In calculating transfer functions for the reactions with the thiocyanate ion, no corrections were applied for a change in ion-association or activity coefficient on changing the solvent. For square planar d^8 systems the reactivity of ion and ion-pair are mostly similar [16].

Figure 2 shows the transfer functions for the platinum(II) complexes and Fig. 3 those of the ligands.

In the Figures the order of the solvents is arbitrarily chosen. Broken lines are introduced for clarity and do not want to suggest any functional relation.

Discussion

Influence of Entering and Leaving Ligand

Only the effect of the leaving group on the reaction rate of the direct (k_2) displacement reaction is straightforward: the pyridine complex is consistently more reactive than the ammonia complex, in line with the order of base strength [10].

The reactivity order of the entering ligands is dependent on both the solvent and the leaving group, as is evident from Table II. This kind of behaviour is irregular for substitutions at square planar platinum(II) compounds, where entering ligands can be arranged in order of nucleophilicity, independent of substrate and solvent, resulting in the quantitative n_{Pt} scale [17]. Deviation from this behaviour has been attributed to a high degree of synchronicity of bond-making and bond-breaking in the transition state [2, 5]. We have observed this kind of behaviour for the palladium(II) complexes of 1-(2-hydroxyphenyl)-3,5-diphenylformazan [3] and it is significant that the same pattern of irregularity is reproduced for the platinum(II) complexes, for which a higher degree of synchronicity is expected [2, 5]. This strengthens our earlier interpretation [3] of the effect of synchronicity as being due to the rigidity of the metal–formazan skeleton, which will decrease the stability of the postulated five-coordinated intermediate. Also the relative inertness of tpp in both palladium(II) [3] and the present platinum(II) formazan reactions may be due to the rigidity of the substrate, resulting in increased steric hindrance towards the bulky tpp ligand. The importance of steric effects is also shown by the fact that the reactions of the platinum complexes with tetramethylthiourea are immeasurably slow. As pointed out [3] an additional factor may be the π-acceptor ability of the formazan system where the strong π-acceptor properties of tpp in the transition state are less important.

Influence of Solvent

Rates of associatively activated substitution reactions at inorganic square planar d^8 complexes vary much less with solvent than S_N2 substitutions at tetrahedral carbon [1, 18]. Our systems also conform to this picture: solvent variation of the rate is not large. Yet the existing differences may clarify the mechanism, if a dissection of solvent effects on initial and transition state is effected [11, 12]. This dissection is displayed in Fig. 1. The general picture is that in spite of the presence of a considerable solvent effect on the transfer chemical potential of the substrate (Fig. 2) and the erratic behaviour of the potential of the entering and leaving (only NH_3 is available) groups (Fig. 3) the transfer chemical potentials of initial and transition states stay close together.

From this general feature we may conclude that the changes in chemical potential on varying the solvent are largely due to general solvation effects that do not change on activation, as special interactions as coordination of solvent donor sites at the axial Pt^{2+} positions are expected to do. This conclusion is reinforced by the fact that in spite of the rather large differences in solubility for the individual compounds, the transfer potentials for $FoPtNH_3$ and FoPtpy are nearly equal in all solvents, while even $\delta_m\mu^{\ominus}$ (FoPttpp) is not much out of the range (Fig. 2).

Appreciable exceptions are only observed for the reactions with the $FoPtNH_3$ substrate in DMSO and DMF. As no difference is observed between the initial state chemical potential for $FoPtNH_3$ and FoPtpy in these solvents we must conclude that the reactivity change in DMSO and DMF is a transition state effect. In addition, it is interesting to observe that to a lesser extent exceptional behaviour is present for reactions in methanol with the entering ligands SCN^- and tu that are stabilized in this solvent compared to tpp (Fig. 3), the reactions of which are not exceptional from the point of reactivity. Although the effect is small, it may be a reminder of the protic *versus* dipolar aprotic distinction of solvents which is of crucial importance in S_N2 reactions at tetrahedral carbon and which is generally absent in square planar d^8 substitutions [1, 18].

Following Parker's hypothesis for tetrahedral carbon [19] we may then put down the destabilization of the transition state compared to the ground state for the cases mentioned in methanol as solvent to partial desolvation of the entering ligands, which is not completely compensated by partial solvation of the leaving ligands. This effect undoubtedly is based on specific (H-bridge) acceptor interaction of the solvent methanol with the donor sites of the ligands. A possible check on the relevance of the acceptor interaction might be obtained by studying halide substitution reactions, but unfortunately the complexes FoPtX (X = Cl, Br, I) are too unstable to be prepared as initial substrates or to be studied as entering ligands as they do not displace NH_3 or py from the formazan complexes.

Accepting the explanation for the small MeOH destabilization means that only the DMSO and DMF exceptions are left to deal with. As mentioned previously [3] these are the solvents with strong donor quantities, as exemplified by the large Gutmann donor numbers [20], 26.6 (DMF) and 29.8 (DMSO). A comparison of substitutions at $FoPtNH_3$ with the corresponding ones at FoPtpy, which are not exceptionally slow (see Fig. 1 and Table II) makes it

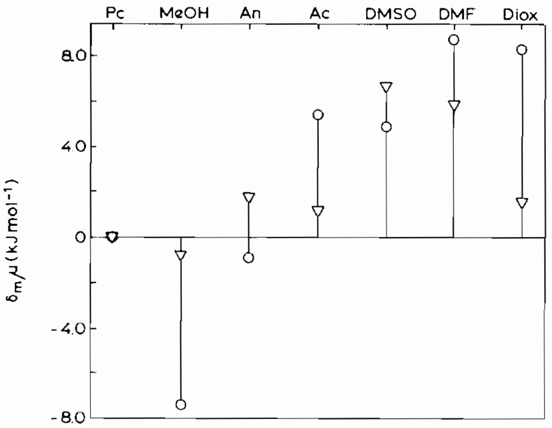

Fig. 4. Position of transfer chemical potential of transition (▽) and final state (○) relative to the initial state for the reaction $FoPtNH_3$ + tpp. Values at 25.0 °C. Reference solvent propylene carbonate.

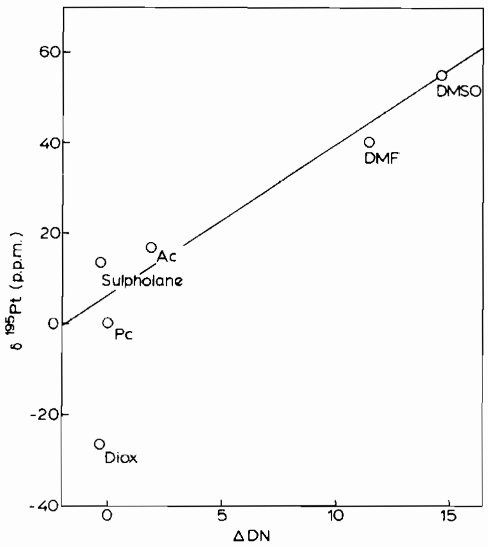

Fig. 5. Downfield ^{195}Pt chemical shift for $FoPtNH_3$, as a function of the solvent Gutmann donor number DN.

clear that desolvation of an exceptionally stabilized initial state on activation cannot be the explanation. It is then obvious to look at electronic effects which are very important factors [9, 10] in determining the stability of the transition state of these associative reactions, characterized by an increased coordination number of the central ion.

We suggest that the phenomenon is due to charge transfer from already solvating solvent molecules to Pt^{2+}, decreasing the positive charge on the metal centre and thus decreasing the reactivity for an associative reaction mode. From the reasons given above this charge-transfer bonding will not add appreciably to the overall free energy of solvation. As no transition-state destabilization effect is found for FoPtpy the most probable mechanism of the charge transfer seems to be a donor interaction of the solvent with the H-atoms of the coordinated NH_3 in $FoPtNH_3$. Alternatively direct bonding of solvent to Pt^{2+} of $FoPtNH_3$ in the transition state could be invoked, which would be sterically hindered in FoPtpy. The last mentioned mechanism seems to be the less probable one, as in no other case an indication of a reactivity lowering of FoPtpy compared to $FoPtNH_3$, based on steric hindrance, is observed. This interpretation means that the position of the transition state on the reaction coordinate will be solvent dependent and that the transfer chemical potential of the transition state will not only be determined by changes in the free energy of solvation. As a result no linear free energy relation is expected for one reaction in different solvents.

A direct equilibrium study of the present reactions is difficult to perform. Therefore we calculated the transfer Gibbs free energy of the final state of the $FoPtNH_3$ + tpp reaction from the transfer functions of the individual compounds. Figure 4 indeed shows $\delta_m\mu^{\neq}$ not to be evenly spaced for different solvents, compared to both initial and final state. Consequently the position of the transition state along the reaction coordinate is solvent dependent.

The explanation of the $FoPtNH_3$ transition state labilization in terms of electronic effects caused by solvent donor interaction with coordinated NH_3 is favoured by the conclusion that for electronic effects appearing in the ^{195}Pt NMR chemical shift of square planar platinum(II) compounds the possibility of the solvent approaching along the z-axis does not seem important [21]. In the light of this conclusion it is interesting to see whether shielding effects operative in determining the magnitude of the NMR chemical shifts are related to the solvent donor number, as observed for ^{23}Na [22] and ^{109}Ag [23] shifts.

Measuring the ^{195}Pt NMR spectra for the platinum complexes under study presented some difficulties because of their very low solubility. Attempts were only successful for $FoPtNH_3$ in a limited number of solvents. Figure 5 shows a good correlation between $\delta(^{195}Pt)$ (negative shielding) and the solvent donor number, with the unexplainable exception of Diox. The fact that the soft donor sulpholane (not included in the rate studies) follows the correlation is a further indication that a direct Pt–solvent bond is not the important factor.

The answer to the question whether the parallel between the relation of donor numbers and ^{195}Pt chemical shifts on the one hand and the one between donor numbers and reactivities on the other hand is rooted in the electronic structure of the solvated

TABLE IV. Regression Parameters for the Rate Constant k_2 of the Direct Displacement.

Substrate	Ligand	p_1	p_2	Multiple Corr. Coeff.
$FoPtNH_3$	tpp	0.40	−0.13	0.95
	tu	0.63	0.11	0.998
	SCN^-	0.49	0.19	0.96
FoPtpy	tpp	0.20	−0.07	0.95
	tu	0.17	0.16	0.99
	SCN^-	0	0.14	0.89

complexes, awaits further development of the quantum mechanical theories concerned.

Empirical Solvent Parameters

In the preceding section the cause for observed exceptionally small reaction rates was sought in either a strong specific acceptor interaction of the solvent with the donor atoms of the entering group or in a specific donor interaction of the solvent with coordinated ammonia. If this conclusion is accepted, we may try to put the conclusion on a more quantitative basis by using a two-parameter equation to explain the complete solvent dependence of the substitution rates:

$$\delta_m\Delta G^{\neq}(k_2) = p_o + p_1\Delta DN + p_2\Delta AN \qquad (7)$$

again with Pc as the reference solvent. For this model we used the Gutmann donor numbers DN [20] and the Gutmann–Mayer acceptor numbers AN [24]. The last mentioned quantities show a good correlation with both Kosower's Z values and Reichart's E_T values [25].

The results of a least-squares regression analysis of the experimental rate constants on the basis of eqn. (7) are summarized in Table IV. The magnitude of the multiple correlation coefficient is impressive. From Table IV it is evident again that donor properties of the solvent are more important for $FoPtNH_3$; no pattern comes forward for the importance of the acceptor properties. It must be emphasized that our model (7) is complex, as the donor factor (p_1) will refer mainly to electronic effects and the acceptor factor (p_2) mainly to solvational effects. Therefore no theoretical prediction of the parameters is possible as yet.

Acknowledgements

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