Initial-state and Transition-state Contributions to Solvent Effects on Reactivity for the Reaction of *cis*-Dichlorobis(4-cyanopyridine)platinum(II) with Thiourea in Binary Aqueous Solvent Mixtures

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Rates, rate laws, and rate constants are reported for the reaction of the title complex *cis*-[Pt(4CN-py)$_2$Cl$_2$] with thiourea, thiocyanate, and iodide in 50% (v/v) methanol, at 298.2 K. From the measured rates of reaction of *cis*-[Pt(4CN-py)$_2$Cl$_2$] with urea and solubilities of these two compounds in a variety of binary aqueous solvent mixtures, the initial-state and transition-state contributions to the reactivity trends have been deduced. For this reaction initial-state effects are considerably more important than transition-state effects.

In the past few decades, sporadic efforts have been made to analyse solvent effects on kinetic parameters into initial-state and transition-state contributions.[1] Such analyses for transition-metal complexes, carried out for several reactions recently,[2] often encounter difficulties in assigning single-ion transfer parameters for charged reactants. One transition-metal complex reaction which avoids this difficulty is that of the square-planar d^8 complex (2,2′-bipyridyl)dichloroplatinum(II), [Pt(bipy)Cl$_2$], with thiourea. Kinetic and thermodynamic data and measurements on this system showed that initial-state solvation effects dominated over transition-state effects in determining reactivity trends.[3] The disappointing feature of this otherwise favourable system is the very low solubility of this platinum(II) complex in water, which prevented the calculation of transfer properties from the normal reference, aqueous medium. We therefore decided to carry out a similar investigation of the reaction of *cis*-dichlorobis(4-cyanopyridine)platinum(II), *cis*-[Pt(4CN-py)$_2$Cl$_2$], with thiourea, since the hydrophilic cyano-groups on the pyridines confer reasonable water solubility on this complex.

We have determined the rates of reaction between *cis*-[Pt(4CN-py)$_2$Cl$_2$] and thiourea in water and in a selection of binary aqueous mixtures. From these kinetic results and appropriate solubility measurements on the two reactants we have analysed the observed reactivity trends into initial-state and transition-state contributions. In this paper we report the results on the reaction of [Pt(bipy)Cl$_2$] with thiourea and compare these with patterns established for other bimolecular reactions involving inorganic complexes in binary aqueous mixtures.

EXPERIMENTAL

The complex *cis*-[Pt(4CN-py)$_2$Cl$_2$] was prepared from K$_2$[PtCl$_4$] (Johnson, Matthey) and 4-cyanopyridine (Koch-Light).[4] Thiourea, potassium thiocyanate, and potassium iodide were AnalaR materials; organic cosolvents were purified by established procedures.[5] Mixed solvents were made up by volume; compositions quoted refer to volume percentages before mixing.

Kinetic runs were carried out in 10-mm silica cells in the thermostatted cell compartment of a Unicam SP 800 or 1800 spectrophotometer. Initial concentrations of the platinum complex were between 1×10^{-4} and 4×10^{-4} mol dm^{-3}; initial concentrations of the nucleophilic reagents are stated in the Tables. Solubilities were determined by equilibrating an excess of thiourea or of the platinum complex with the appropriate mixed solvent. Aliquots were removed and either evaporated to dryness (thiourea) or immediately diluted and analysed by atomic absorption spectroscopy (platinum complex), using a Perkin-Elmer 360 instrument.

RESULTS

Substitution kinetics for *cis*-[Pt(4CN-py)$_2$Cl$_2$] have not previously been described. We have therefore established the reactivity pattern for the nucleophiles iodide, thiosulphate, and thiourea, in 50% (v/v) methanol solution (Table 1). The substitution kinetics are consistent with the normal rate law, equation (1), for square-planar d^8

$$-\mathrm{d}[\mathrm{Pt(4CN\text{-}py)_2Cl_2}]/\mathrm{d}t = (k_1 + k_2[\text{nucleophile}])[\mathrm{Pt(4CN\text{-}py)_2Cl_2}] \quad (1)$$

complexes. Here, as for other similar complexes, the k_2 value is considerably larger for thiourea than for iodide or thiosulphate; compare, for example, substitution at *trans*-[Pt(py)$_2$Cl$_2$].[6] The $k_{\text{obs.}}$ values quoted in Table 1 are consistent with a common k_1 value of 1.2×10^{-4} s^{-1}. In fact k_1 values are 1.1×10^{-4}, 1.2×10^{-4}, and 1.3×10^{-4} s^{-1} for thiourea, thiosulphate, and iodide respectively (50% methanol; 298.2 K).

At the relatively high concentrations of nucleophiles used, the kinetics of substitution in the various solvents are dominated by the second-order term in the rate law; the k_1 term of equation (1) is nearly negligible. Observed

TABLE 1

Mean observed first-order rate constants, $k_{\text{obs.}}$,[a] and derived second-order rate constants, k_2, for the reaction of *cis*-[Pt(4CN-py)$_2$Cl$_2$] with nucleophiles in 50% (v/v) aqueous methanol,[b] at 298.2 K

	[Nucleophile]/mol dm^{-3}					
	0.02	0.04	0.06	0.08	0.10	k_2[c]
	$10^3k_{\text{obs.}}$/s^{-1}					dm^3 mol^{-1} s^{-1}
Iodide		0.27	0.34	0.40	0.51	0.0036 ±0.0005
Thiosulphate	0.28	0.48	0.64	0.81	0.98	0.0087 ±0.0002
Thiourea	2.5	4.6	6.5	9.1	11.7	0.115 ±0.004

[a] Each value of $k_{\text{obs.}}$ represents the mean of two independent determinations. [b] Composition by volume before mixing. [c] Error limits cited are standard deviations.

TABLE 2

Mean observed first-order rate constants, $k_{obs.}$,[a] and derived second-order rate constants, k_2, for the reaction of *cis*-[Pt(4CN-py)$_2$Cl$_2$] with thiourea in binary aqueous solvent mixtures,[b] at 298.2 K

Solvent	[thiourea]/mol dm^{-3}					k_2[c]/dm^3 mol^{-1} s^{-1}
	0.02	0.04	0.06	0.08	0.10	
	$10^3k_{obs.}$/s^{-1}					
Water	7.7	9.9	16.8	20.8	27	0.25 ± 0.02
Methanol: 25%	4.7	8.2	10.8	13.0	16.7	0.145 ± 0.008
50%	2.5	4.6	6.5	9.1	11.7	0.115 ± 0.004
Tetrahydrofuran: 25%	0.68	1.53	2.6	3.6	4.3	0.045 ± 0.001
50%	0.31	0.63	0.99	1.40	1.83	0.019 ± 0.000 4
Acetonitrile: 50%	0.36	0.70	1.08	1.51	1.99	0.020 ± 0.000 5
Dimethyl sulphoxide: 50%	4.4	8.3	12.6	19.7	21.2	0.225 ± 0.016

[a] Each value of $k_{obs.}$ represents the mean of two independent determinations. [b] Solvent compositions by volume before mixing. [c] Error limits cited are standard deviations.

first-order rate constants and derived second-order rate constants for the reaction of *cis*-[Pt(4CN-py)$_2$Cl$_2$] with thiourea in water and in various binary aqueous solvent mixtures are reported in Table 2.

Solubilities of the platinum complex and of thiourea are reported in Table 3.

TABLE 3

Solubilities of [Pt(4CN-py)$_2$Cl$_2$] and of thiourea in water and in binary aqueous solvent mixtures * at 298.2 K

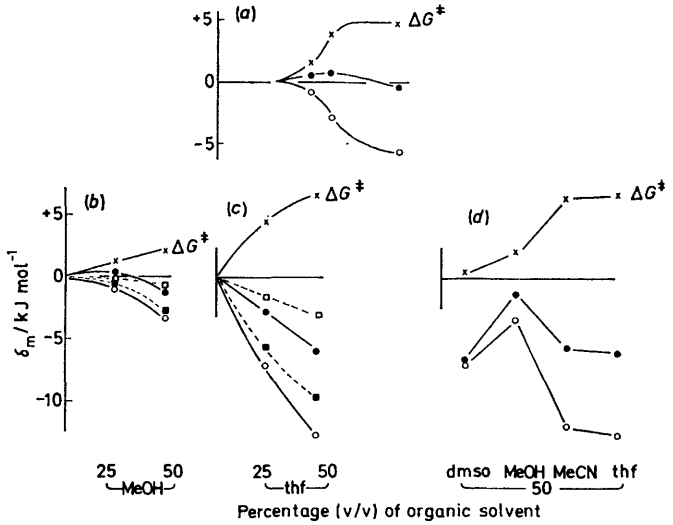
(Co)solvent	% (v/v)	Solubility/mol dm^{-3}	
		[Pt(4CN-py)$_2$Cl$_2$]	thiourea
Water		0.000 34	1.92
Methanol	25	0.000 42	2.19
	50	0.001 05	2.33
Acetonitrile	50	0.026	3.17
Dimethyl sulphoxide	50	0.002 5	4.54
Tetrahydrofuran	25	0.003 1	
	50	0.016	

* Solvent compositions by volume before mixing.

DISCUSSION

The analysis of results into initial-state and transition-state effects was carried out in the same manner as described for the reaction of [Pt(bipy)Cl$_2$] and thiourea.[3] Transfer functions for the reactants, initial state, and transition state, in all cases from water, on the molar scale, are set out in Table 4, and plotted in the Figure. Reactivity trends for *cis*-[Pt(4CN-py)$_2$Cl$_2$] plus thiourea are dominated by initial-state solvation and chemical potential changes; the initial state is generally affected by about twice as much as the transition state on transfer from water to the binary aqueous mixtures we have used in the present investigation. In turn the initial-state effects arise predominantly from the chemical potential changes of the platinum(II) complex, rather than those for the thiourea.

There is a marked difference between the present *cis*-[Pt(4CN-py)$_2$Cl$_2$] reaction with thiourea and that of [Pt(bipy)Cl$_2$] previously described. In the [Pt(bipy)Cl$_2$] case, transition-state chemical potential changes were very small (see Figure), and rate trends were thus determined almost exclusively by initial-state changes. For the 4-cyanopyridine case, the transition-state



The variation with solvent composition of the chemical potentials of the initial (○) and transition (●) states for the reactions of (*a*) [Pt(bipy)Cl$_2$] and (*b*)—(*d*) *cis*-[Pt(4CN-py)$_2$Cl$_2$] with thiourea. (□) and (■) indicate the chemical potentials of thiourea and of Pt^{II} respectively. thf = Tetrahydrofuran, dmso = dimethyl sulphoxide

TABLE 4

Analysis of solvent effects on reactivity into initial-state and transition-state effects for the reaction of [Pt-(4CN-py)$_2$Cl$_2$] with thiourea (298.2 K)

	Cosolvent (% v/v)[a]					
	MeOH		MeCN	dmso	thf	
	25	50	50	50	25	50
$\delta_m\mu^{\ominus}$ (Pt^{II})/kJ mol^{-1}	−0.51	−2.78	−10.7	−4.88	−5.46	−9.53
$\delta_m\mu^{\ominus}$ (thiourea)/kJ mol^{-1}	−0.33	−0.48	−1.24	−2.13	−1.55[b]	−3.04[b]
$\delta_m\mu^{\ominus}$ (initial state)/kJ mol^{-1}	−0.84	−3.26	−11.94	−7.01	−7.01	−12.54
$\delta_m\Delta G^{\ddagger}$/kJ mol^{-1}	+1.20	+2.02	+6.36	+0.41	+4.35	+6.62
$\delta_m\mu^{\ddagger}$/kJ mol^{-1}	+0.37	−1.24	−5.58	−6.60	−2.66	−5.92

[a] Solvent compositions by volume before mixing. [b] Calculated from data of C. Treiner and P. Tzias, *J. Solution Chem.*, 1975, **4**, 471.

changes, although smaller than initial-state changes, are still significant. The only difference is the presence or absence of the hydrophilic cyano-substituents. The difference in pattern must therefore be attributed to these, although how the observed difference arises thence is not clear.

It is interesting to compare our conclusions on the above reactions with published observations on closely related substitution reactions of *trans*-$[Pt(py)_2Cl_2]$, in dimethyl sulphoxide–water mixtures.[7] Rates of reaction with bromide increase as the proportion of dimethyl sulphoxide increases, but rates of reaction with thiourea decrease as the proportion of dimethyl sulphoxide increases. These opposed trends can be rationalised to a considerable extent by reactant chemical potential trends, for the chemical potential of bromide presumably increases (*cf.* chloride [8]) and that of thiourea decreases (*cf.* Table 2), as the proportion of dimethyl sulphoxide increases. The relative importance of initial-state and transition-state solvation in substitution reactions of transition-metal complexes, indeed in substitution reactions in general, depends greatly on the system. Our conclusions on the relatively greater importance of initial-state solvation changes in determining reactivity trends for these platinum(II) complexes are put into context [2] and discussed [9] elsewhere.

We are grateful to Thorn Lighting Limited for the loan of a platinum lamp for atomic absorption spectroscopy measurements, to the Royal Society for a Grant-in-aid for the purchase of the SP 800 spectrophotometer, to the S.R.C. for their support, and to Dr. B. G. Cox for the communication of chloride-ion transfer parameters prior to publication.

[8/1901 *Received*, 31*st October*, 1978]

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