Solvent Effects on the Initial and Transition States for the Reaction of 2,2'-Bipyridyldichloroplatinum(II) with Thiourea in Aqueous Dioxan and in Aqueous Tetrahydrofuran†

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Rates of reaction of 2,2'-bipyridyldichloroplatinum(II) with thiourea are reported for a series of water–1,4-dioxan and water–tetrahydrofuran solvent mixtures, at 293.2 and 298.2 K respectively. From an analysis of these kinetic results and data on the solubilities of the reactants, it is demonstrated that initial-state solvation changes play a predominant role in determining the reactivity trends for this reaction in the solvent mixtures studied.

It is possible to estimate the relative importance of solvent effects on the initial and transition states in determining kinetic parameters for a reaction from knowledge of the solvation of the reactants and kinetic data. A detailed analysis of reactions of tetra-alkyltin compounds with mercury(II) chloride in methanol–water solvent mixtures showed that the large changes in reaction rates with change in solvent composition could be ascribed almost entirely to changes in reactant solvation.[1] A similar conclusion was reached concerning the Menschutkin reaction of trimethylamine with methyl iodide,[2] and the solvolysis of t-butyl chloride in water-rich mixtures.[3] On the other hand, in demetallation of tetra-alkyl-lead compounds with iodine, solvent effects in the transition state are of comparable importance to solvent effects in the initial state in determining reactivity.[4]

The extension of such an analysis of solvent effects on reactivities to transition-metal complexes is often difficult. In particular, since most of the reactions of interest involve charged species one usually has to face the problem of estimating solvation characteristics for single ions. One way round this difficulty is to examine the difference between the reactivity trends for two similar complexes of identical charge, as in the aquation of the substituted tris(1,10-phenanthroline) complexes $[Fe(5NO_2\text{-phen})_3]^{2+}$ and $[Fe(4,7Me_2\text{-phen})_3]^{2+}$ in water–t-butyl alcohol mixtures.[5] But to obtain information on one specific reaction it is necessary to estimate the thermodynamic solvation parameters involved, which can be done with a greater or lesser degree of confidence depending on the circumstances. This approach has been used with some success for the reaction of the $[Fe(bipy)_3]^{2+}$ (bipy = 2,2'-bipyridyl) cation with cyanide ion in several series of mixed aqueous solvents.[6] In this case the effects of changing the solvent composition on the chemical potential of the large iron(II) complex are likely to be much less than those on the chemical potential of the small cyanide ion. Indeed the small variation in rates of the dissociative[7] aquation of iron(II) complexes with solvent composition[6,8] is consistent with small solvent effects on the chemical potentials of these cations. The variation in chemical potential of the cyanide ion with solvent composition can be estimated with some confidence *via* that for chloride ion,[9] and has been found to be

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[1] M. H. Abraham, G. F. Johnston, J. F. C. Oliver, and J. A. Richards, *Chem. Comm.*, 1969, 930; M. H. Abraham, *J. Chem. Soc.* (*A*), 1971, 1061.

[2] M. H. Abraham, *Chem. Comm.*, 1969, 1307.

[3] S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1957, **79**, 5937; E. M. Arnett, P. McC. Duggleby, and J. J. Burke, *ibid.*, 1963, **85**, 1350; E. M. Arnett, W. G. Bentrude, and P. McC. Duggleby, *ibid.*, 1965, **87**, 2048.

[4] M. H. Abraham, *J.C.S. Perkin II*, 1972, 1343.

[5] J. Burgess, *J. Chem. Soc.* (*A*), 1968, 1085, 2728.

[6] M. J. Blandamer, J. Burgess, and J. G. Chambers, *J.C.S. Dalton*, 1976, 606.

[7] J. M. Lucie, D. R. Stranks, and J. Burgess, *J.C.S. Dalton*, 1975, 245.

[8] M. J. Blandamer, J. Burgess, and R. I. Haines, *J.C.S. Dalton*, 1976, 385.

[9] C. F. Wells, *J.C.S. Faraday I*, 1973, 984; 1975, 1868; Y. Pointud, J. P. Morel, and L. Avedikian, *Electrochim. Acta*, 1974, **19**, 229.

the dominant factor in determining reactivity variations for the reaction of the $[Fe(bipy)_3]^{2+}$ cation with cyanide ion.[6] It is instructive here to compare the large variation in reactivity with solvent composition for this associative reaction with the small variation for the dissociative interchange reaction of $Fe^{3+}(aq)$ with thiocyanate.[10] For the latter reaction the large increase in the chemical potential of the thiocyanate anion on transfer from water to dimethyl sulphoxide is not reflected in a large increase in the rate of reaction. In principle the analysis of solvent effects on initial and transition states should be more satisfactory for reactions of uncharged metal complexes. For instance the reaction of rhenium pentacarbonyl iodide, $[Re(CO)_5I]$, with cyanide ion should be more amenable to this type of analysis than that of the $[Fe(bipy)_3]^{2+}$ cation with cyanide ion. Unfortunately our efforts to separate solvent effects on the reaction of $[Re(CO)_5I]$ with cyanide ion into initial- and transition-state contributions foundered on the large uncertainties in the chemical potentials of the cyanide ion in the organic-rich solvent mixtures in which the kinetics could be monitored.[11]

TABLE 1

Average first-order rate constants, $k_{obs.}$, and derived first- and second-order rate constants k_1 and k_2 [defined by equation (2) of text], for the reaction of $[PtCl_2(bipy)]$ with thiourea in water + tetrahydrofuran solvent mixtures (mole fraction x_2 tetrahydrofuran) at 298.2 K

					$10^3k_1/s^{-1}$	$k_2/dm^3\ mol^{-1}\ s^{-1}$
$x_2 = 0.510$						
[thiourea]/mol dm^{-3}	0.025	0.050	0.075	0.100	*ca.* 1	0.20 ± 0.01
$10^3k_{obs.}/s^{-1}$	4.6	9.1	13.4	19.6		
$x_2 = 0.200$						
[thiourea]/mol dm^{-3}	0.025	0.035	0.050	0.070	*ca.* 2	0.32 ± 0.02
$10^3k_{obs.}/s^{-1}$	12	15	19	25		
$x_2 = 0.143$						
[thiourea]/mol dm^{-3}	0.010	0.020	0.030	0.040	*ca.* 1	0.71 ± 0.04
$10^3k_{obs.}/s^{-1}$	6.8	15	21	29		
$x_2 = 0.098$						
[thiourea]/mol dm^{-3}	0.0033	0.0100	0.0133	0.0167	*ca.* 2	1.27 ± 0.13
$10^3k_{obs.}/s^{-1}$	6.3	16	18	24		

Obviously, therefore, a satisfactory transition-metal complex system will consist of an uncharged complex and an uncharged entering ligand, with both kinetic parameters and solubilities (or other sources of information concerning the dependence of chemical potential on solvent composition) measurable over a suitable range of solvent mixtures. Platinum(II) chemistry seems a likely source of suitable reactions. In the present paper we report an analysis of solvent effects on reactivity for the substitution (1) (tu = thiourea), in water–dioxan and in water–tetrahydrofuran mixtures. We suggest that here changes in reactivities are determined mainly by reactant solvation effects.

$$[PtCl_2(bipy)] + tu \longrightarrow [PtCl(bipy)(tu)]^+ + Cl^- \quad (1)$$

EXPERIMENTAL

2,2′-Bipyridyldichloroplatinum(II) was prepared by the published method.[12] Kinetic runs were carried out in 10-mm silica cells in the thermostatted cell compartment of a Unicam SP 800A recording spectrophotometer. Solubilities of the platinum complex were determined by equilibrating an excess of it with solvent mixtures of appropriate composition, and then estimating the concentration of dissolved complex spectrophotometrically by monitoring optical densities at 310 and 380 nm.

RESULTS

Kinetics.—Runs were conducted with thiourea in large excess, under which conditions all the runs followed first-order kinetics over at least three half-lives. There was an isosbestic point at 360 nm in all the solvent mixtures. Rate constants were computed from absorbances at 310 and 380 nm, corresponding to the appearance of the product and disappearance of the starting complex respectively. For a given run, identical rate constants were obtained from absorbance changes at the two wavelengths.

Computed first-order rate constants, $k_{obs.}$, for the reaction in water–tetrahydrofuran mixtures at 298.2 K are reported in Table 1. These results are consistent with the usual two-term rate law for substitution at square-planar complexes, equation (2). Values of k_1 and k_2 for each solvent mixture are also given in Table 1. The k_1 values in Table 1

$$-d[PtCl_2(bipy)]/dt = (k_1 + k_2[tu])[PtCl_2(bipy)] \quad (2)$$

are subject to considerable uncertainty as this path makes only a small contribution to the overall reaction at the thiourea concentrations used. We are concerned with the associative k_2 path, so the small k_1 values are hereafter ignored. The k_1 terms for the reaction in water–dioxan make an even smaller contribution to overall $k_{obs.}$ values under the conditions used; k_2 values for the reaction in these solvent mixtures were therefore obtained directly by dividing $k_{obs.}$ by the concentration of thiourea (0.010 mol dm^{-3}). These k_2 values for the reaction in water–tetrahydrofuran are listed in Table 2.

Solubilities.—The measured solubilities of $[PtCl_2(bipy)]$ in water–dioxan mixtures at 293.2 K and in water–tetrahydrofuran mixtures at 298.2 K are reported in Table 2.

Transfer Functions.—A key consideration in this study was the calculation of transfer quantities describing the

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[10] D. H. Devia and D. W. Watts, *Inorg. Chim. Acta*, 1973, **7**, 691.

[11] M. J. Blandamer, J. Burgess, S. J. Cartwright, and M. Dupree, *J.C.S. Dalton*, 1976, 1158.

[12] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1934, 965.

TABLE 2

Solubilities (S) of [$PtCl_2$(bipy)], second-order rate constants (k_2) for the reaction of [$PtCl_2$(bipy)] with thiourea, and transfer functions $\delta_m\mu^\ominus$ and $\delta_m\Delta G^\ddagger$ for reactants and reaction, in mixed aqueous solvents containing mole fraction x_2 of organic component. For each of the two series of solvent mixtures the transfer parameters refer to transfer from the mixture of lowest x_2 (*cf.* text)

Dioxan (293.2 K)					
x_2	0.050	0.083	0.124	0.175	0.241
$\delta_m\mu^\ominus$(tu)/kJ mol^{-1}	0	−0.052	−0.097	−0.181	−0.199
10^5S[$PtCl_2$(bipy)]/mol dm^{-3}	7.0	9.3	16.7	29.3	40.2
$\delta_m\mu^\ominus$[$PtCl_2$(bipy)]/kJ mol^{-1}	0	−0.71	−2.16	−3.55	−4.33
$\Sigma\delta_m\mu^\ominus$(reactants)/kJ mol^{-1}	0	−0.76	−2.26	−3.73	−4.53
k_2/dm^3 mol^{-1} s^{-1}	2.5	2.0	1.35	0.90	0.50
$\delta_m\Delta G^\ddagger$/kJ mol^{-1}	0	+0.54	+1.50	+2.49	+3.93
Tetrahydrofuran (298.2 K)					
x_2	0.097	0.143	0.200	0.510	
$\delta_m\mu^\ominus$(tu)/kJ mol^{-1}	0	−0.66	−1.20	−2.06	
10^5S[$PtCl_2$(bipy)]/mol dm^{-3}	31	33	61	90	
$\delta_m\mu^\ominus$[$PtCl_2$(bipy)]/kJ mol^{-1}	0	−0.16	−1.70	−2.67	
$\Sigma\delta_m\mu^\ominus$(reactants)/kJ mol^{-1}	0	−0.82	−2.90	−4.73	
k_2/dm^3 mol^{-1} s^{-1}	1.27	0.70	0.27	0.20	
$\delta_m\Delta G^\ddagger$/kJ mol^{-1}	0	+1.48	+3.83	+4.61	

change in chemical potential of the complex and thiourea in their solution standard states, $\delta_m\mu^\ominus$, as the composition of the liquid mixture was altered. Thus, for example, with reference to thiourea, $\delta_m\mu^\ominus$(tu) in equation (3) represents the change in chemical potential in the solution standard state on going from a mixture where the mole fraction of water is x_1' to another mixture of mole fraction x_1. Similar expressions can be written for the platinum complex and transition state.

$$\delta_m\mu^\ominus(\text{tu}) = \mu^\ominus(\text{tu},x_1) - \mu^\ominus(\text{tu},x_1') \qquad (3)$$

It follows that the change in the activation Gibbs function, $\delta_m\Delta G^\ddagger$ [equation (4)] is given by equation (5). Values of $\delta_m\Delta G^\ddagger$ can be obtained from the rate constants for reaction in the two mixtures, $k(x_1)$ and $k(x_1')$, using equation (6).

$$\delta_m\Delta G^\ddagger = \Delta G^\ddagger(x_1) - \Delta G^\ddagger(x_1') \qquad (4)$$

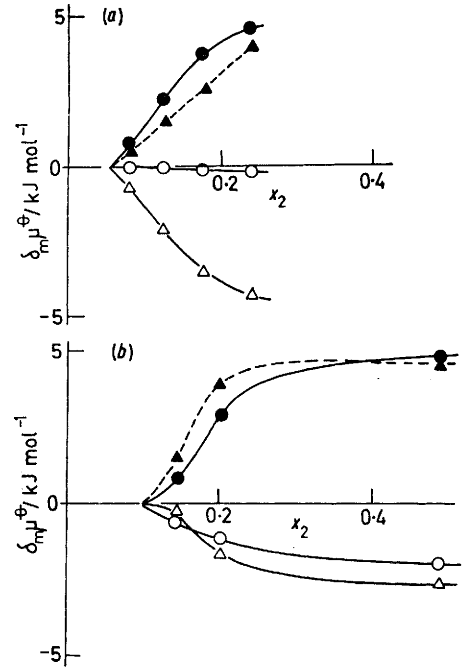
$$\delta_m\Delta G^\ddagger = \delta_m\mu^\ddagger - \delta_m\mu^\ominus\,(\text{complex}) - \delta_m\mu^\ominus(\text{tu}) \qquad (5)$$

$$\delta_m\Delta G^\ddagger = -RT \ln k(x_1)/k(x_1') \qquad (6)$$

In most studies the reference system corresponds to the situation where $x_1' = 1$, *e.g.* solubilities in the mixtures are compared with those in water. However, the solubility of the platinum complex in water was too low for satisfactory spectrophotometric determination of rate constants for reaction with thiourea. We therefore had to calculate the transfer functions using as our reference an aqueous mixture. For both water–tetrahydrofuran and –dioxan, we report in Table 2 these functions with reference to the most water-rich solvent mixture in each case. Thus for water–tetrahydrofuran mixtures $x_1' = 0.913$, [*cf.* equations (3) and (4)], and for water–dioxan mixtures, $x_1' = 0.950$ (Table 2), so that the δ_m functions indicate the effect of changing x_1 relative to the mol fraction x_1' of the reference system.

The transfer functions $\delta_m\mu^\ominus$(complex) for the platinum complex were calculated from measured solubilities. The related functions for thiourea in water–dioxan mixtures were calculated from published solubilities.[13] Treiner and Tzias[14] reported values of $d\mu^\ominus(\text{tu})/dx_1$ for eight water–tetrahydrofuran mixtures over the range $0.4902 < x_1 < 0.9866$ at 298 K. The value of $d\mu^\ominus(\text{tu})/dx_1$ at $x_1 = 1$ was calculated by fitting the dependence of $d\mu(\text{tu})/dx_1$ on x_1 over the range $0.9412 < x_1 < 0.9866$ to equation (7) using a least-squares technique. In the same computer program (FORTRAN for a Cyber 72 computer), the computed value of $d\mu^\ominus(\text{tu})/dx_1$ at $x_1 = 1$ was combined with the values of this quantity at other mol fractions to evaluate the required transfer functions $\delta_m\mu^\ominus$(tu), equation (3), using a numerical integration technique.

$$d\mu^\ominus(\text{tu}) = a + bx_1 + cx_1^2 \qquad (7)$$



Variation of chemical potentials of the reactants and the transition state for the reaction of [$PtCl_2$(bipy)] with thiourea, in (*a*) water–dioxan at 293.2 K and (*b*) water–tetrahydrofuran at 298.2 K: (●) $\Sigma\delta_m\mu^\ominus$(reactants); (▲) $\delta_m\Delta G^\ddagger$; (○) $\delta_m\mu^\ominus$(tu); (△) $\delta_m\mu^\ominus(Pt^{II})$

DISCUSSION

The solubilities both of [$PtCl_2$(bipy)] and of thiourea increase as the proportion of the non-aqueous component

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[13] E. Angelescu and F. Cornea, *Ann. Univ. C.I. Parhon Bucuresti, Ser. Stiint. Nat.*, 1957, **15**, 87.

[14] C. Treiner and P. Tzias, *J. Solution Chem.*, 1975, **4**, 471.

increases, both in water–dioxan and in water–tetrahydrofuran mixtures. The rate of the reaction between [$PtCl_2$(bipy)] and thiourea decreases as the proportion of non-aqueous component increases in both series of solvent mixtures. The relations between these observations are indicated in Table 2 and in the Figure. Both the Table 2 values and the Figure show that the major factor determining reaction rates in these systems is the change in chemical potential of the reactants, $\Sigma\delta_m\mu^{\ominus}$(reactants) in Table 2. Solvent effects on the chemical potential of the transition state are of less importance. In the water–dioxan mixtures we have studied, the change in chemical potential with solvent composition is much greater for [$PtCl_2$(bipy)] than for thiourea, hence it is the variation in solvation of the complex which is the most important factor in controlling reaction rates. In the water–tetrahydrofuran mixtures, which incidentally cover a much wider range of solvent composition, solvation effects on the chemical potentials both of the platinum complex and of the thiourea make significant contributions to reactivity variation. The predominant role played by initial-state solvation in the reaction of [$PtCl_2$(bipy)] with thiourea here is analogous to that in reactions of tetra-alkyltin compounds with mercury(II) chloride and in the Menschutkin reaction of trimethylamine with methyl iodide.

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