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The use of free energy relationships to rationalise structural and solvent effects on the photoreduction of cobalt(III) complexes in aqueous organic solvent medium

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Quantum yields for the photoreduction of a series of Co^{III} complex ions, [CoClen$_2$ (RC$_6$H$_4$NH$_2$)]$^{2+}$ where R=*p*-OMe, *p*-OEt, *p*-Me, *m*-Me, H and *p*-F using a low pressure Hg vapour lamp (254 nm) in aqueous ethanol mixtures (15–40% v/v organic cosolvent), increase with increase in mole fraction of the cosolvent in the binary solvent mixture under investigation. The Hammett correlation is linear, affording negative reaction constants, which indicate that the excited state is electron deficient. Correlation of the quantum yield data with Kamlet–Taft's solvatochromic parameters indicates that the specific solvent–solute interactions play a dominant role in governing the reactivity.

Keywords: cobalt(III) complexes, photoreduction, solvent effect, Hammett equation

Introduction

The study of the influence of solvent on the reactions of cobalt(III) complexes in mixed solvent media and correlation of reaction rates with various solvent and structural parameters afford important mechanistic information.[1-6] Accumulated information on the correlation of reaction rates with the properties of the solvent through linear solvation energy relationships (LSER) has led to some significant results. The general belief is that solvent characteristics, such as hydrophobic effects, preferential solvation, anion and cation solvating tendencies and hydrogen bond donor–acceptor influences on the kinetics and energetics of the redox reaction of cobalt(III) complexes, is important in elucidation of mechanisms. In spite of the observation that single empirical parameters can be used as good approximations of solvent polarity, no single macroscopic physical parameter could possibly account for the multitude of solute–solvent interactions on the molecular microscopic level.[7] Thus, bulk solvent properties like relative permittivity,[8] solvent ionizing power,[9] and/or dipolarity/polarisability[10] will poorly describe the microenvironment around the reacting species, which governs the stability of the intermediate complex and hence the rate of the reaction. Therefore, during the recent past a variety of attempts have been made to quantify different aspects of solvent polarity and then to use the resultant parameters to interpret solvent effects on reactivity through multiple regression analysis. Various treatments for the above solvent–solvent–solute interactions based on LSER have been developed. [11] Although the separation of solvent effects into various solvent–solvent–solute interaction mechanisms is purely formal, the multiparameter approach to solvent effects has been shown to work well.[12]

Structural variation studies give a much better insight into the nature of the transition state and the mechanism of the redox reaction. Most of the work in this area has dealt with complexes of the pentammine class, emphasis being placed on the dependence of reaction rates upon the nature of the sixth ligand.[13] I now extend the approach of using correlation analysis technique to the description of solvent and substituent effects on photoreduction of a series of cobalt(III) complex ions in aqueous mixtures of ethanol.

Experimental

The cobalt(III) complexes, [CoClen$_2$(RC$_6$H$_4$NH$_2$)]Cl$_2$ where R = *p*-OMe, *p*-OEt, *p*-Me, *m*-Me, H, and *p*-F, were prepared and purified according to the standard literature procedures.[14] Analytical quality reagents were generally used. Solutions for photolysis contained the cobalt(III) complex (4x10^{-3}M), and NaNO$_3$ (0. 1M). All the solutions prepared contained binary solvents of varying compositions: ethanol in water [15-40% (v/v) of co-solvent]. Steady photolysis experiments were carried out using a low pressure mercury vapour pen-ray quartz lamp (254 nm). Air-equilibrated solutions were used for photolysis and the temperature control was maintained at 25±1°C. For quantum yield determinations photolysis was carried out to less than *ca* 15% of the total reaction. The incident light intensities were measured by potassium ferrioxalate actinometry.[15] Quantum yields were calculated by estimating cobalt(II) formed by Kitson's method.[16] All absorption measurements were carried out using a Shimadzu UV-vis double beam spectrophotometer.

Correlation analyses were made using Microcal origin (version 3. 5) computer software. The goodness of the fit was established using correlation coefficient, *r*, standard deviation, SD and Exner's statistical parameter, ψ. The relative importance (on a percentage scale) of different solvation effects were analysed using various empirical solvent parameters. The percentage contribution of a parameter to the total effect of reactivities was determined. To calculate this value the regression coefficient of each parameter is statistically quantified as described in the literature.[5]

Results and discussion

The quantum yields, measured at 254 nm, for the photo-reduction of all the coblat(III)-aryl amine complexes in various water–ethanol mixtures are presented in Table 1. In the solvent mixture investigated $\Phi_{Co(II)}$ increased as the mole fraction of the organic co-solvent increased. Attempts have been made to analyse the effect of solvent and substituent on the photoreduction quantum yields of the cobalt(III)-aryl amine complexes using linear and multiple regression equations.

Solvent–reactivity correlation

The influence of solvent relative permittivity, ε_r, on the photo-reduction quantum yield can be described by the equation of Laidler and Eyring:[8]

$$\mathrm{d} \ln k/d(1/\varepsilon_r) = e^2 Z^2 (1/\mathrm{r} - 1/r^*)/2kT \qquad (1)$$

where k is the rate constant ($\Phi_{Co(II)}$ in the present study), Z the net charge, r the effective radius and r^* the radius of the activated species. The correlation of log $\Phi_{Co(II)}$ with inverse of relative permittivity in the solvent mixture studied showed satisfactory results ($0.994 \geq r \geq 0.972$, $0.034 \geq$ SD ≥ 0.019, $0.29 \geq \psi \geq 0.13$, straight lines with positive

Table 1 Quantum yields (10$^2\Phi$) for the photoreduction of [CoClen$_2$(RC$_6$H$_4$NH$_2$)]Cl$_2$ in air-equilibrated water–ethanol mixtures at 25±1°C

	Ethanol % (v/v)					
R	15	20	25	30	35	40
p-OMe	3. 78	4. 43	5. 17	5. 98	6. 75	6. 92
p-OEt	3. 24	3. 88	4. 29	5. 56	6. 21	6. 64
p-Me	2. 72	2. 77	3. 81	4. 24	5. 08	5. 45
m-Me	2. 03	2. 43	3. 07	3. 14	4. 24	4. 98
H	1. 52	1. 81	1. 95	2. 52	3. 01	4. 02
p-F	1. 09	1. 37	1. 58	1. 78	2. 12	2. 83

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slopes). The positive slope indicates that the excited state is less polar than the reactant. Such an excited state will more easily be attained in a medium of lower relative permittivity and hence the increase in quantum yield with increase in the mole fraction of organic co-solvent is observed.

Winstein and his coworkers[9] suggested treating solvent effects on rates in terms of Eqn (2).

$$\log k = \log k_o + mY \qquad (2)$$

Where, *m* is a substrate parameter measuring the substrate sensitivity to changes in the ionising power of the medium and *Y*, the solvent ionising power, is a parameter characteristic of the given solvent. The plots of log $\Phi_{Co(II)}$ versus *Y* were linear, for all the cobalt(III) complexes, with negative slopes ($0.997 \geq r \geq 0.949$, $0.042 \geq$ SD ≥ 0.014, $0.39 \geq \psi \geq 0.09$). The negative values of *m* indicate that the excited state is less polar than the reactant which will more easily be attained in a medium of lower ionising power and hence the increase in quantum yield with increase in the mole fraction of organic co-solvent is observed.

The simplicity of idealised electrostatic models for the description of solvation of ions and dipolar molecules, considering solvents as nonstructured continuum, has led to the use of physical constants, such as relative permittivity, ε_r, refractive index, *n*, or functions thereof, as macroscopic solvent parameters for the evaluation of medium effects. However, solute–solvent interactions take place on a molecular microscopic level within a structured discontinuum consisting of individual solvent molecules, capable of mutual solvent–solvent interactions. For this reason, and because of neglecting specific solute–solvent interactions, the electrostatic approach to medium effects often failed in correlating observed solvent effects with physical solvent parameters. In reality, satisfactory quantitative descriptions of medium effects have taken into account all nonspecific and specific solvent–solvent–solute interactions. The separation of solvent polarity into nonspecific and specific solvent–solvent–solute interaction mechanisms is purely formal, but, if this separation can be reasonably done, the resultant parameters may be used to interpret solvent effects through such multiple correlations, thus providing information about the type and magnitude of interactions with the solvent.[7]

This kind of dual dependency of reactivity on solvent composition is illustrated by the Kamlet–Taft solvatochromic comparison method.[10] This method may be used to unravel, quantify, correlate and rationalise multiple interacting solvent effects on reactivity. Thus, the experimentally measured quantum yield values, $\Phi_{Co(II)}$, for the photoreduction of $[CoClen_2(RC_6H_4NH_2)]^{2+}$ ions were correlated with the solvatochromic parameters α, β and π* characteristic of the different solvent mixtures in the form of the linear solvation energy relationship:

$$\log k = A_o + s\pi^* + a\alpha + b\beta \qquad (3)$$

where, π* is an index of solvent dipolarity/polarisability, which measures the ability of the solvent to stabilise a charge or a dipole by virtue of its dielectric effect, α is the solvent hydrogen bond donor (HBD) acidity which describes the ability of the solvent to donate a proton in a hydrogen bond, β is the solvent hydrogen bond acceptor (HBA) basicity which provides a measure of the solvent's ability to accept a proton (donate an electron pair) in a solute-to-solvent hydrogen bond and A_o is the regression value of the solute property in the reference solvent cyclohexane. The regression coefficients *s*, *a* and *b* measure the relative susceptibilities of the solvent dependent solute property log $\Phi_{Co(II)}$ to the indicated solvent parameter. These solvatochromic parameters for the aqueous organic mixtures used in the present study were calculated as described in the literature.[5]

The $\Phi_{Co(II)}$ values in different water–ethanol mixtures show an excellent correlation, when compared to those obtained using macroscopic solvent parameters such as ε_r and Y, via the above LSER with an observed variance of *ca* 98%. The statistical results of the correlation and weighted percentage contributions of the solvatochromic parameters are presented in Table 2. The observation of this multiple regression analysis leads to the following preliminary conclusions. (i) The weighted percentage contributions of the solvatochromic parameters indicate that the specific solute–solvent interactions, as indicated by P_α and P_β, play a major role in governing the reactivity of the complexes. (ii) The contribution of the solvent HBD acidity, α, to the total solvent effect is dominant. This may be due to the fact that, though both water and ethanol are amphiprotic, the enhanced water structure when small amounts of alcohol are added has a larger HBD capability, but smaller HBA ability, than the common water structure.[17] Hence, increase in mole fraction of the added co-solvent in the mixture may stabilise the excited state, to a greater extent, through specific solute–solvent interactions and consequently increase the rate of the reaction. (iii) The sign of the coefficients *s*, *a* and *b* of the triparametric equation is randomly observed, that is, all the observations of a particular set of experiments do not result in value with similar sign. This means that the medium interacts in a complex manner with the reactant/excited state.[1]

A dynamic exchange of solvent molecules exists between the solvation shell of the excited state and the bulk.[18] As the mole fraction of organic co-solvent increases in the mixture, more and more organic solvent molecules are introduced into the solvation shell, thereby increasing the hydrophobic environment of the excited state, consequently lowers the energy of LMCT band. Increase in hydrophobicity of the medium stabilises the excited state (which is less polar than the reactant as indicated by Laidler–Eyring and Grunwald–Winstein correlations) through specific solute-solvent interactions and consequently increases the reduction quantum yield as the mole fraction of organic co-solvent in the mixture increases. This is demonstrated by the observation that, for all the cobalt(III) complexes under investigation a plot of log $\Phi_{Co(II)}$ versus mole fraction of the organic co-solvent is linear with positive slope and a representative curve is shown in Fig. 1.

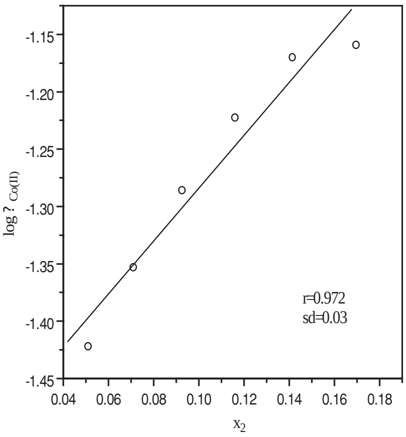

Fig. 1 Plot of log $\Phi_{Co(II)}$ versus mole fraction of the organic co-solvent x_2 for the photoreduction of $[CoClen_2(p\text{-}OMeC_6H_4NH_2)]^{2+}$ ion in water–ethanol mixture.

Table 2 Statistical results, coefficients and weighted contributions of solvent parameters in Kamlet–Taft equation for the photoreduction of $[CoClen_2(RC_6H_4NH_2)]Cl_2$ complexes in water–ethanol mixtures

R in ligand	R^2	SD	ψ	*s*	*a*	*b*	P_{π^*}	P_α	P_β	Observed variance 100 r^2		
										Eyring	Winstein	Kamlet
p-OMe	0.973	0.027	0.23	151	–219	62	35	51	14	94	90	97
p-OEt	0.982	0.026	0.19	162	–260	41	35	56	09	96	92	98
p-Me	0.984	0.026	0.18	152	196	525	17	22	60	94	91	98
m-Me	0.980	0.033	0.20	–76	126	2	37	63	–	97	96	98
H	0.990	0.024	0.14	–56	–41	–144	23	17	60	99	99	99
p-F	0.998	0.009	0.06	–67	–245	–391	09	35	56	98	98	99.8

R^2, coefficient of multiple determination; SD-standard deviation; ψ, Exner's statistical parameter; *s*, *a* and *b*, coefficients of equation (3); P_{π^*}, P_α and P_β weighted percentage contributions.

Table 3 Statistical results from the plot of log $\Phi_{Co(II)}$ against Hammett's substituent constants for the photoreduction of $[CoClen_2(RC_6H_4NH_2)]Cl_2$ in aqueous ethanol mixtures

	Ethanol %(v/v)					
	15	20	25	30	35	40
r	0. 991	0. 991	0. 980	0. 995	0. 980	0. 966
SD	0. 031	0. 029	0. 046	0. 023	0. 044	0. 042
ψ	0. 16	0. 16	0. 24	0. 12	0. 24	0. 32
ρ	–1. 542	–1. 450	–1. 492	–1. 541	–1. 432	–1. 064

r, correlation coefficient; SD, standard deviation; ψ, Exner's statistical parameter; ρ, reaction constant.

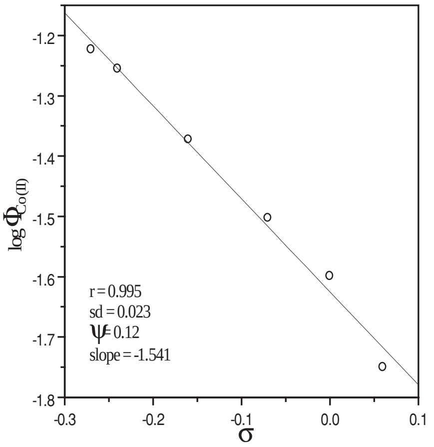

Fig. 2 Hammett's plot of log $\Phi_{Co(II)}$ versus σ for the photoreduction of $[CoClen_2(RC_6H_4NH_2)]^{2+}$ ion in 30% (v/v) water–ethanol mixture.

Structure-reactivity correlation

To gain more information regarding the nature of the excited state and hence the mechanism, the quantum yield for photoreduction of a series of $[CoClen_2(RC_6H_4NH_2)]^{2+}$ ions were estimated, in binary solvent mixtures, by varying the substituent, R, in the $RC_6H_4NH_2$ ligand. Analysis of the data in Table 1 reveals that variation of $\Phi_{Co(II)}$ is systematic. Electron releasing substituents increase $\Phi_{Co(II)}$ while electron withdrawing ones decrease it. The reactivity pattern is brought out by correlation of log $\Phi_{Co(II)}$ with Hammett's substituent constants, σ. A satisfactory correlation is obtained and a representative Hammett plot is shown in Fig. 2. The reaction constants, ρ, and statistical data at different volume fractions of the added organic co-solvent are recorded in Table 3. The reaction constants are large and negative. Thus, the formation of a strongly electron deficient reaction centre in the excited state is indicated. Such an excited state will be stabilised by electron releasing substituents and hence increase in the rate of reduction.

It is clear that ρ values, like log $\Phi_{Co(II)}$ values for given reactants, are influenced by solvent effects. Hammett predicted that, in general, the reaction constants appear to increase with decreasing relative permittivity of the medium. In the present study, in line with the above prediction, ρ increases as ε_r decreases. This may be due to the fact that the transmission of the polar effects of the substituents through the surrounding medium increases in importance relative to transmission through the molecular cavity as ε_r is decreased. [11]

It may be concluded that, UV excitation (254 nm) of the cobalt(III)–aryl amine complexes in air-equilibrated solutions causes bleaching of its intense ligand-to-metal charge transfer excited states with concurrent production of cobalt(II) ions. The $\Phi_{Co(II)}$ increase with increasing mole fraction of organic co-solvent in the binary mixture studied. The correlation of reaction rate with solvatochromic parameters indicates that the specific solute-solvent interaction plays a dominant role on the reactivity. Hammett correlation indicates that the formation of an electron deficient excited state during the photoreduction of the cobalt(III)–aryl amine complexes under investigation.

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