Preliminary Note

Solvent effect and activation parameters for the photoinduced electron transfer between Ru(bpy)$_3$$^{2+}$ and aromatic amines

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1. Introduction

Excited-state electron transfer reactions have been the subject of many studies during the last years [1]. Among the most used agents in these processes, tris(2,2'-bipyridine)ruthenium(II) (Ru(bpy)$_3$$^{2+}$) has played a prominent role. In its excited state it can act as an electron acceptor or donor [2, 3] depending upon the redox potential of the partner in the redox couple. Detailed kinetic studies have been carried out on the relationship between the rate constants for electron transfer and the free energy change of the process. Activation parameters were also determined for the reductive [4, 5] and oxidative [5] quenching of Ru(bpy)$_3$$^{2+}$ luminescence. In all cases the results were interpreted with the Rehm–Weller formalism [6] using the Marcus–Husch [7] electron transfer theory.

However, there are still some features of these processes which are not clearly explained with the commonly used models. Thus, for example, in a previous paper [8] we reported a large influence of the solvent on the quenching rate constants of Ru(bpy)$_3$$^{2+}$ by naphthylamines. This solvent effect also becomes apparent when a comparison is made of the results for the similar quenching process by other aromatic amines in methanol (MeOH) [4] and acetonitrile (CH$_3$CN) [5]. For these two solvents of similar polarity the rate constants differ in some cases by more than one order of magnitude.

In this preliminary note we report the determination of the activation parameters for reductive quenching by aromatic amines in MeOH and CH$_3$CN and in mixtures of varying composition. It is found that while the rate constants and activation enthalpies change with the amine, the activation entropy is only a function of the solvent and can be related to its structural changes on forming the transition state.

2. Experimental details

Ru(bpy)$_3$$^{2+}$ was a gift from Dr. G. Ferraudi. The quenchers were commercially available and were purified by standard procedures.

Static luminescence measurements and lifetime determinations were carried out as described previously [8].

TABLE 1

Rate constants and activation parameters for the photoinduced electron transfer between excited $Ru(bpy)_3^{2+}$ and aromatic amines

Amine	Acetonitrile			Methanol		
	$k_q(25\,°C)$ $(M^{-1}\,s^{-1})$	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (entropy units)	$k_q(25\,°C)$ $(M^{-1}\,s^{-1})$	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (entropy units)
DMA	9.5×10^7	2.2	-14.6	1.6×10^8	3.3	-10.0
1NA	1.6×10^8	2.2	-13.6	2.0×10^9	1.9	-9.4
2NA	2.1×10^7	3.1	-14.2	3.6×10^8	2.8	-9.8

DMA, dimethylaniline; 1NA, 1-naphtylamine; 2NA, 2-naphtylamine.
Estimated errors are ±5% for rate constants and ±10% for activation parameters.

3. Results and discussion

Bimolecular quenching rate constants k_q were obtained from Stern–Volmer constants and lifetime data as a function of temperature. The values in CH_3CN were well below the diffusion limit. In MeOH a correction for the diffusional effect [9] was applied, assuming a value of 1.2×10^{10} M^{-1} s^{-1} for the diffusional rate constant in this solvent (this is a mean value of literature data for molecules of similar complexity; see, for example, ref. 10) and a functional dependence on temperature of the form T/η (where η is the viscosity).

The rate constants at 298 K and activation parameters are given in Table 1. The data are expressed in terms of the transition state theory:

$$k_q = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{\neq}}{R}\right) \exp\left(-\frac{\Delta H^{\neq}}{RT}\right)$$

From the data in Table 1 it can be seen that in a given solvent, even when rate constants vary widely, the activation entropy is approximately the same for all the quenchers studied. Our results for DMA coincide, within the experimental error, with those reported by other workers in both solvents [4, 5].

When these results are compared with those of Baggott [4] for other aromatic amines in MeOH it can be seen that the activation entropies are always in the range -7 to -10 entropy units for all the quenchers. Kitamura et al. [5] also measured the $\Delta S^{\neq}$ in CH_3CN for the quenchers N-methylaniline and dimethyl-p-toluidine, obtaining -14.2 entropy units and -14.4 entropy units respectively. It can be concluded that for these two solvents the activation entropy for the reductive quenching is only a function of the solvent.

When an attempt is made to interpret these results in the light of Marcus's electron transfer theory [7] for an outer-sphere mechanism, the main difficulty which arises is how to take into account large differences in

rate parameters for solvents with very similar dielectric properties, such as MeOH and CH_3CN. We think that the problem can be traced to the fact that the model does not consider the structural organization (*i.e.* hydrogen bonding) of the solvent.

A macroscopic property related to the bulk solvent organization is the viscosity. We have also determined the activation parameters for the quenching of $Ru(bpy)_3^{2+}$ by DMA and 1NA in several CH_3CN–MeOH mixtures. In Fig. 1 $\Delta S^{\neq}$ is plotted against the solvent composition and it can be seen that it follows the same trend as the viscosity. The activation entropy remains nearly constant in the range 50 - 100 wt.% CH_3CN where the viscosity shows only a minor change. Then it increases with viscosity as the solvent becomes richer in MeOH.
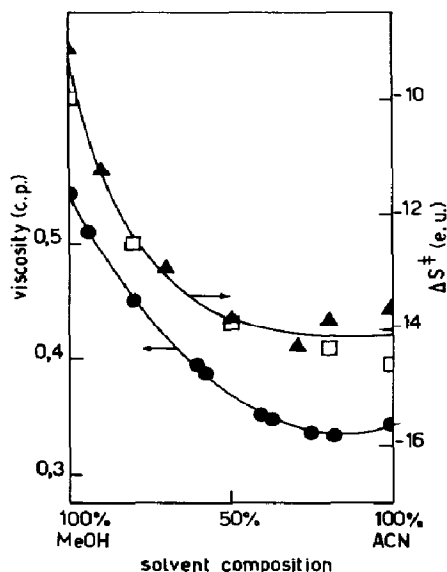

Fig. 1. Plot of activation entropies ($\square$, DMA; $\blacktriangle$, 1NA) and viscosity ($\bullet$) *vs.* solvent composition (in weight percent) for CH_3CN–MeOH mixtures.

This correspondence between $\Delta S^{\neq}$ and viscosity probably reflects the fact that MeOH is ordered by hydrogen bonding, and that the entropy loss on forming the transition state is compensated for by the rupture of the solvent structure. In the case of CH_3CN the lack of hydrogen bonding gives place to a more negative activation entropy.

Further work is in progress in order to see if this behaviour is common to other electron transfer processes and solvent systems.

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