

## Non-Diffusive Photo-electron Transfer in Various Solutions. The Effect of Solvents on the Reaction Rates in the Marcus Inverted and Normal Regions.

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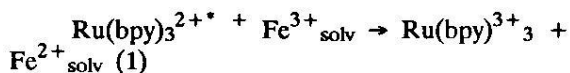
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**Summary:** Nano-second laser flash photolysis data on electron-transfer between Ru (bpy)<sub>3</sub><sup>2+</sup> and Fe<sup>3+</sup> in a number of C<sub>1</sub> to C<sub>10</sub> n-alkanols at room temperature are interpreted in terms of the Perrin Kinetics and the first-order perturbation theory formalisms. Experimental values of the Frank-Condon factors increase with decreasing  $\lambda$  (the solvent reorganization energy) in the normal region ( $\lambda > -\Delta G^\circ$ ), pass through a maximum around  $\lambda = -\Delta G^\circ$  and then decrease with decreasing  $\lambda$  in the inverted region ( $\lambda < -\Delta G^\circ$ ). These observations are in excellent agreement with the Marcus theory of electron-transfer.

The theories of electron-transfer originating from the pioneering work of Marcus [1-5] predict an inversion in the rate vs  $\Delta G^\circ$  or rate vs  $\lambda$  plots for  $\lambda < -\Delta G^\circ$ , where  $\lambda$  is the solvent reorganization energy and  $\Delta G^\circ$  is the standard free-energy change of the reaction. Few published reports provide some evidence concerning the existence of this region [6]. In this report we describe data that are in close agreement with Marcus theory in both the inverted and the normal regions.

Using the method of flash photolysis we studied the following reaction



between the solvated ferric ions,  $\text{Fe}^{3+}_{\text{solv}}$ , and the excited state of Tris (bipyridyl) ruthenium,  $\text{Ru}(\text{bpy})_3^{2+*}$  as a function of  $\lambda$  in a series of n-alkanols (C<sub>1</sub>-C<sub>10</sub>). Details of experimental set up and method of data analysis are available elsewhere [7]. The  $\Delta G^\circ$  of reaction 1 remains constant (1.5 eV) in all the alkanols. Effect of solvents on  $\Delta G^\circ$  as calculated by using a published method [8] were found to be negligible  $\pm 0.05$  eV. On the contrary, the  $\lambda$  values systematically decrease from 2.4 eV in methanol (C<sub>1</sub>) to 1.3 eV in decanol (C<sub>10</sub>). The  $\lambda$  values were obtained as sum of the inner-sphere (eq. 10 of ref. 9) and the outer-sphere contributions [10].

We analyzed our data in terms of first-order perturbation theory and the Perrin type kinetics [11]. Briefly, the first-order specific rate,  $k_{\text{obs}}$ , ac-

cording to the first-order perturbation theory formalism is given by:

$$k_{\text{obs}}(\text{R}) = \frac{2\pi}{\hbar} [\text{H}(\text{R})]^2 F \quad (2)$$

where, R is center to center electron-transfer distance,  $[\text{H}(\text{R})]$  is the electron exchange matrix element, and F the Franck-Condon-weighted density of state is given by:

$$F(\lambda) = (4\pi\lambda k_{\text{T}})^{-1/2} \exp \left[ -\frac{(\Delta G^\circ + \lambda)^2}{4\lambda k_{\text{T}}} \right] \quad (3)$$

An experimentally useful form of eq. (2) is [12]:

$$k_{\text{obs}}(\text{R}) = \tau^{-1} = \nu_{\text{obs}} \exp \left[ -\frac{(\text{R}-\text{R}_0)}{a} \right] \quad (4)$$

where  $\tau$  is the mean life of the excited state in the presence of a quencher,  $\text{R}_0$  is the distance of closest approach, and  $a$  is a constant. Furthermore,  $\nu_{\text{obs}}$  ( $\text{s}^{-1}$ ) stands for:

$$\nu_{\text{obs}} = \frac{2\pi}{\hbar} [\text{H}(\text{R}_0)]^2 F \quad (5)$$

In obtaining eq. (4) and eq. (5) we have utilized the fact that:

$$[\text{H}(\text{R})] = [\text{H}(\text{R}_0)] \exp \left[ -\frac{(\text{R}-\text{R}_0)}{a} \right] \quad (6)$$

The Perrin kinetics [11], eq. 7, allows the procurement of data on R as a function of the quencher concentration, [Q],

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$$R = \frac{[3000 \ln P]^{1/3}}{4\pi N_A [Q]} \quad (7)$$

where the probability of survival of the excited state,  $P$ , is given by the ratio of the mean life time of the excited species in the absence ( $\tau_0$ ) and the presence ( $\tau$ ) of a quencher.

A plot of  $(R-R_0)$  vs  $\ln k_{obs}$  allows the determination of  $\lambda_{obs}$  and using these values in eq. (5) one can get the experimental Franck - Condon factors provided  $[H(R_0)]$  values are available. Given that the electron-transfer takes place via a solute-solvent cage charge - transfer complex [9], one can estimate the matrix elements using a simple theory [13] according to which,  $[H(R_0)] = (\mu^2/\epsilon_{eff} R_0^3)$ , where,  $\mu$  is the dipole moment of the solvent medium,  $\epsilon_{eff}$  is the effective dielectric constant of the medium [14] and  $R_0$  is given by  $r_1 + r_2$  with  $r_1 = 7.1 \text{ \AA}$  (the radius of  $Ru(bpy)_3^{2+}$ ) and  $r_2$  being the sum of the crystal radius of  $Fe^{3+}$  ( $0.60 \text{ \AA}$ ) and the length of carbon chain on the alcohol,  $L_{al}$ , solvating  $Fe^{3+}$ . Values of  $L_{al}$  were obtained from molar volume data [15] are given in Table-1 which also compiles the experimental values of  $\nu_{obs}$  and  $F_{exp}$  [16] together with all the parameters of n-alkanols needed for various calculations.

Table-1: Various parameters for n-alkanols ( $\epsilon$ ,  $n$ ,  $\mu$ , and  $L_{al}$ ), the solvent reorganization energies ( $\lambda$ ), the observed frequency factors ( $\nu_{obs}$ ), the calculated and the experimental Franck-Condon factors ( $F_{calc}$  and  $F_{exp}$ )

| n-Alkanol       | $\epsilon$ | $n$   | $\mu$<br>Debye | $L_{al}$<br>( $\text{\AA}$ ) | $\lambda$<br>(ev) | $\lambda^*$<br>(ev) | $\nu_{obs}$<br>$10^7 s^{-1}$ | $F_{exp}$<br>(ev) | $F_{calc}$<br>(ev) |
|-----------------|------------|-------|----------------|------------------------------|-------------------|---------------------|------------------------------|-------------------|--------------------|
| C <sub>4</sub>  | 17.1       | 1.399 | 1.66           | 6.26                         | 1.92              | 1.87                | 8.0                          | 0.53              | 0.63               |
| C <sub>5</sub>  | 13.9       | 1.409 | 1.64           | 6.98                         | 1.84              | 1.70                | 7.3                          | 0.68              | 1.09               |
| C <sub>6</sub>  | 13.3       | 1.418 | 1.55           | 7.38                         | 1.75              | 1.61                | 6.7                          | 0.93              | 1.30               |
| C <sub>7</sub>  | 11.4       | 1.424 | 1.54           | 7.64                         | 1.25              | 1.53                | 5.7                          | 0.89              | 1.44               |
| C <sub>8</sub>  | 10.3       | 1.429 | 1.53           | 7.92                         | 1.21              | 1.46                | 4.4                          | 0.79              | 1.46               |
| C <sub>9</sub>  | 9.1        | 1.433 | 1.52           | 8.22                         | 1.20              | 1.38                | 3.7                          | 0.76              | 1.36               |
| C <sub>10</sub> | 7.8        | 1.437 | 1.51           | 8.42                         | 1.18              | 1.29                | 3.0                          | 0.68              | 1.12               |

a) Reference 17, b) Reference 15.

Calculated values of  $F$ ,  $F_{calc}$ , are also included in Table-1 for comparison with  $F_{exp}$ . For a better comparison  $F_{calc}$  and  $F_{exp}$  are plotted against  $\lambda$  in Fig. 1. The agreement between theory (solid curve) and experiment (circles), though qualitative, is quite good and in our opinion is an unambiguous proof of the Marcus theory in both the normal and the inverted regions. Quantitatively,  $F_{obs}$  values are about 1.5 times smaller than  $F_{calc}$  and this discrepancy is largely attributable to an estimate of  $\lambda$

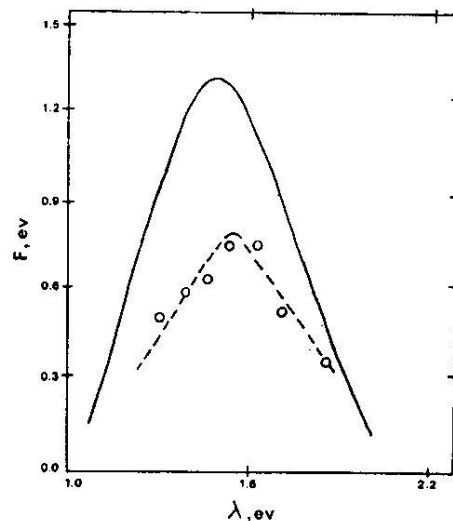


Fig.1: Plots of  $F_{calc}$  vs  $\lambda$  (solid line),  $F_{exp}$  vs  $\lambda$  (circles), and  $F_{exp}$  vs  $\lambda^*$  (dotted line) for the photoelectron-transfer reaction in C<sub>4</sub>-C<sub>10</sub> n-alkanols at room temperatures.

values. The true values of  $\lambda$  that harmonize the theory and the experiment are also included in Table-1 as  $\lambda^*$ . The dashed line in Fig. 1 is the theoretical curve estimated using  $\lambda^*$  values.

Our data on electron-transfer rates in C<sub>1</sub>-C<sub>3</sub> alkanols [16] strictly obey the Stern-Volmer kinetics and the observed second-order specific rate ( $6.2 \pm 0.8 \times 10^8 M^{-1} S^{-1}$  in C<sub>1</sub>,  $4.4 \pm 0.5 \times 10^8 M^{-1} S^{-1}$  in C<sub>2</sub>, and  $3.3 \pm 0.5 \times 10^8 M^{-1} S^{-1}$  in C<sub>3</sub>) thus obtained are inversely proportional to  $\eta$  (where,  $\eta$  is the viscosity of the solvent) indicating that the electron-transfer in these alcohols involve diffusive mechanism. On the otherhand, our data in C<sub>4</sub>-C<sub>10</sub> n-alkanols are best represented by the Perrin kinetics rather than the Stern-Volmer kinetics. Furthermore, second-order specific rates ( $2.4 \pm 0.5 \times 10^8 M^{-1} S^{-1}$  in C<sub>4</sub> - C<sub>10</sub>) in these alcohols are very much insensitive to  $\eta$  indicating the non-diffusive nature of electron-transfer in C<sub>4</sub>-C<sub>10</sub> alkanols.

In past the failure to observe the inverted region for electron-transfer in solutions has been attributed to a number of factors [6]. In particular, masking by diffusion was considered to be the main cause of the failure of the Marcus theory. In our opinion the highly viscous nature of C<sub>4</sub>-C<sub>10</sub> alkanols precludes diffusion together of the reactants and is thereby responsible for the observance of the inverted region in our work. Furthermore, we have

also studied the reaction of solvated electrons using pulse radiolysis method with a number of aromatic hydrocarbons [17] and ferric ions in C<sub>1</sub>-C<sub>10</sub> alkanols and all these data show trends similar to those outlined above.

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