AN ALTERNATIVE APPROACH ON ELECTRON TRANSFER MECHANISM OF THE FLUORESCENCE QUENCHING OF 3-CARBOXY-5,6-BENZOCOUMARIN BY SOME AROMATIC AMINES

Cristina TABLET,[a] Magda FIFIRIG[b] and Mihaela HILLEBRAND[a*]

[a] Fac. of Chemistry, Dept. of Physical Chemistry, University of Bucharest, Bd. Regina Elisabeta, 4-12, Bucharest, RO-030018, Roumania
[b] Fac. of Chemistry, Dept. of Physics and Applied Mathematics, University of Bucharest, Bd. Regina Elisabeta, 4-12, Bucharest, RO-030018, Roumania

The previous data on the fluorescence quenching of a coumarin derivative, 3-carboxy-5,6-benzocoumarin by electron transfer reaction from some aromatic amines are reanalyzed in terms of the Tachiya model, emphasizing the role of the diffusion mediated second order reaction rate. The model was applied considering a distance dependent electron transfer rate constant and, either fixed or distance dependent diffusion constant. It was found, that in order to properly fit the experimental data for ΔG^0 values in the normal Marcus region, an ultrafast electron transfer process must be assumed at short acceptor-donor distances.

INTRODUCTION

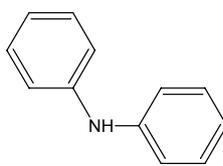In a previous paper we have reported a steady state fluorescence study on the fluorescence quenching of a coumarin derivative, 3-carboxy-5,6-benzocoumarin (Fig.1) by some aromatic amines in acetonitrile.[1]
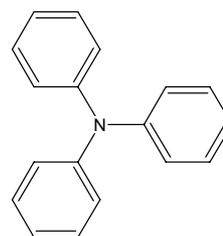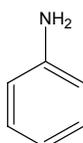
Acceptor: Donors:
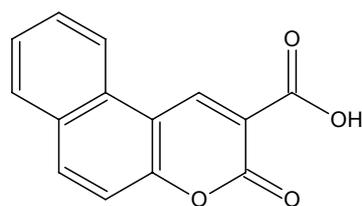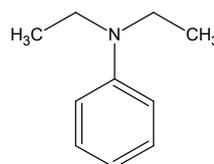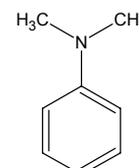

Fig. 1 – Structural formula of the the investigated systems.

* Corresponding author: mihh@gw-chimie.math.unibuc.ro

The bimolecular quenching constants were determined by a Stern-Volmer analysis. The results were rationalized in terms of an electron transfer (ET) from the amines (the donors) to the excited S_1 state of the acceptor. According to the Marcus theory,[2] the rate constant for the electron transfer reaction, k_{et}, was calculated by the formula:

$$k_{et} = \upsilon \times exp\left(\frac{-\Delta G^*}{k_B T}\right) \quad (1)$$

where

$$\Delta G^* = \frac{\left(\Delta G^0 + \lambda\right)^2}{4 \times \lambda} \quad (2)$$

In the above equations, υ is the frequency factor, ΔG^* and ΔG^0 represent the free energy of activation and the free energy change for the ET reaction, respectively, and λ stands for total reorganization energy given by the sum of the internal reorganization energy, λ_{in} and the solvent reorganization energy, λ_S:

$$\lambda = \lambda_{in} + \lambda_S \quad (3)$$

ΔG^0 was calculated using the Rehm-Weller formula,[3]

$$\Delta G^0 = E\left(\frac{D}{D^+}\right) - E\left(\frac{A}{A^-}\right) - E_{00} - \frac{e^2}{\varepsilon(r_D + r_A)} \quad (4)$$

where $E(D/D^+)$ and $E(A/A^-)$ represent the oxidation and reduction potentials of the donor and acceptor, respectively, E_{00} the excitation energy of the acceptor and r_D, r_A the radius of the two partners.

As our experimental data were insufficient for the fit to a theoretical model, we have also included in the plot $\ln k$ - ΔG^0, the literature data for other coumarin derivatives (C151, C500, C481, C522, C153) with eight aromatic amines (aniline, methylaniline, ethylaniline, dimethylaniline, diethylaniline, diphenylamine and triphenylamine).[4] The best fit of the experimental points is characterized by λ = 0.79 eV, $\upsilon = 1.53 \times 10^{12}$ s^{-1} and $k_d = 1.34 \times 10^{10}$ M^{-1}s^{-1}.

Another analysis of the fluorescence quenching in donor-acceptor systems in terms of the ET processes was made by Tachiya.[5,6] Instead of assuming that the electron transfer occurs only at a fixed donor-acceptor distance as in the Marcus model, the new treatment developed by Tachiya[5] considers the role of the diffusion mediated second order reaction rate. The aim of the present work is a comparison of the experimental data for the electron transfer constants for the same coumarin derivatives-aromatic amines systems as before and the results obtained considering the second-order ET rate constant ks.

THEORETICAL MODELS AND COMPUTATIONAL DETAILS

The Marcus formula for nonadiabatic ET is given by equation:

$$k = \frac{4\pi^2}{h} \times \frac{J^2}{(4\pi k_B T \lambda)^{1/2}} exp\left[\frac{-(\Delta G^0 + \lambda)^2}{4 k_B T \lambda}\right] \quad (5)$$

in which J represents the coupling element, the overlap between the ground and the excited state and the other quantities have the previously discussed meaning.

In the framework of the dielectric continuum model, λ is given by equation (6):

$$\lambda = \frac{e^2}{2}\left(\frac{1}{n^2} - \frac{1}{\varepsilon}\right) \times \left(\frac{1}{r_D} + \frac{1}{r_A} - \frac{2}{R}\right) \quad (6)$$

where e is the electronic charge, n and ε are the refractive index and the dielectric constant of the solvent, respectively, and R the intermolecular donor-acceptor distance.

$$J = J_0 \times exp(-\beta(R - (r_D + r_A)/2)) \quad (7)$$

In cases of weak coupling J is estimated by an exponential dependence on the intermolecular R distance Tachiya *et al.*[5] showed that the Marcus formula gives the first order rate, valid only assuming a fixed internuclear R distance and that in some cases the second order diffusion mediated rate constant must be considered, as given by eq. (8):

$$k_s = \frac{1}{c_\infty}\int_{r_D + r_A}^{\infty} k(R) \times c(R) \times 4\pi R^2 dR \quad (8)$$

In eq.(8), c(R) represents the donor concentration at the distance R of the acceptor and c_∞, the concentration in the bulk of the solution.

Considering the diffusion equations under the approximation of the closure:

$$\frac{1}{k_s} = \frac{1}{k_{eq}} + \frac{1}{k_D} \quad (9)$$

where k_{eq} and k_D are given by eqs. (10) and (11) respectively:

$$k_{eq} = \int_{r_D + r_A}^{\infty} 4\pi R^2 \times k(R)\, dR \qquad (10)$$

$$k_D = \frac{4\pi \times D \times \left[\displaystyle\int_{r_D + r_A}^{\infty} k(R) \times R^2\, dR \right]^2}{\displaystyle\int_{r_D + r_A}^{\infty} k(R')(R')^2\, dR' \left[\frac{1}{R'} \int_{r_D + r_A}^{R'} k(R) \times R^2\, dR + \int_{R'}^{\infty} k(R)R\, dR \right]} \qquad (11)$$

The rate constants, k_s and k_D were obtained by numerical calculations as functions of ΔG^0 using numerical codes written in Fortran 77.

RESULTS AND DISCUSSION

The second order rate constant, k_s, was calculated with equation (9), using several approximations and values of the parameters.

As a first step k_{eq} was calculated by eq. (10), the distance dependent rate constant, $k(R)$ being evaluated by means of eq. (5). Plotting the dependence $k(R)$ – R for two ΔG^0 values, -1.5 eV, -1 eV, (Fig. 2), we emphasize the decreasing with

six orders in the magnitude of k in the range of R, 6-20 Å.

Due to the above mentioned decreasing of k we have decided to use R = 20 Å as the superior limit in the radial integral entering in the numerical evaluation of either k_{eq} or k_D.

The reorganization energy, eq.(6), was calculated for acetonitrile, using n = 1.3440 and ε = 37.5. The values for the parameters J_0 and β were those generally recommended, J_0 = 50 cm^{-1} and 100 cm^{-1}, β = 1A^{-1}.[5,6] We have considered averaged values for the acceptor and donors radius, $r_D = r_A$ = 3 Å.
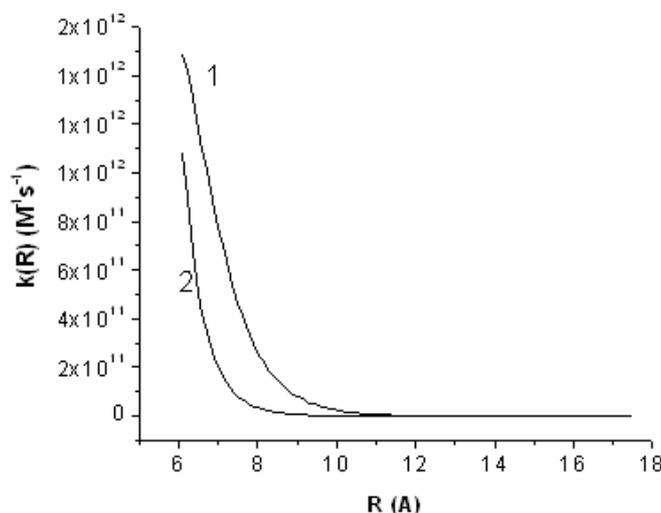

Fig. 2 – Dependence k(R) - R for two ΔG^0 values, (1) -1.5 eV, (2) -1 eV.

In this simple model, instead of calculating k_D by eq.(11) two values were used in the range of recommended values, i.e., k_D= 1.4×10^{10} M^{-1}s^{-1} and k_D= 2.2×10^{10} M^{-1}s^{-1}.[5,6] The results are plotted in Figs. 3 and 4 for the two values mentioned for J_0. From Fig. 3 we can observe that for a given value of J_0 and different k_D, starting from ΔG^0 about –0.5 eV the values of k_s tend to a common value.

Inspecting Fig. 4, we can also note that J_0=100 cm^{-1} is more appropriate to the experimental results.

In the second step, the diffusion rate constant was evaluated using eq. (11), the theoretical dependence being also displayed in Fig. 3 as plot 3.
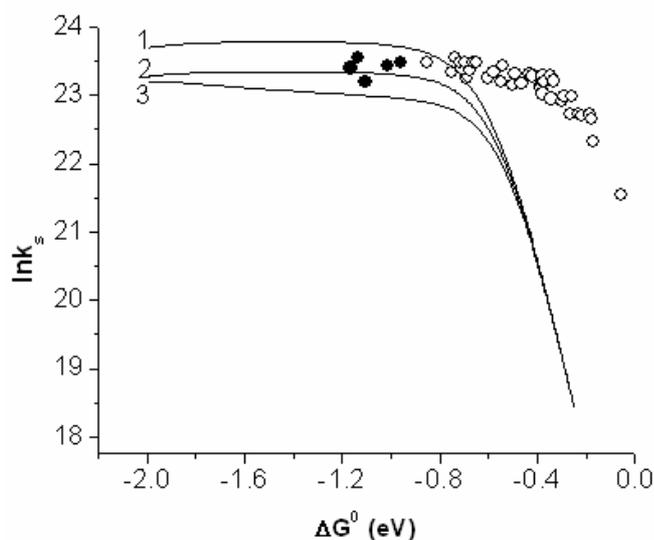
Fig. 3 – Dependence of the bimolecular quenching constants on the change in the free energy of the electron transfer reaction. Filled squares represent our values, open circles represent literature data[4] for related other coumarin derivatives. The lines represent the plot of the theoretical second order diffusion mediated rate constant, ks (eqs. (9) and (10), J_0= 100 cm^{-1}) vs. the change in the free energy, ΔG^0 for k_D= 1.4×10^{10} M^{-1}s^{-1} (1) , k_D= 1.34×10^{10} M^{-1}s^{-1}(2) and k_D estimated by eq.(11) (3).

Fig. 4 – Same plots as in Fig. 3 for k_D= 1.34×10^{10} M^{-1}s^{-1} and two J_0 values, J_0= 100 cm^{-1}(1) and J_0= 50 cm^{-1} (2).
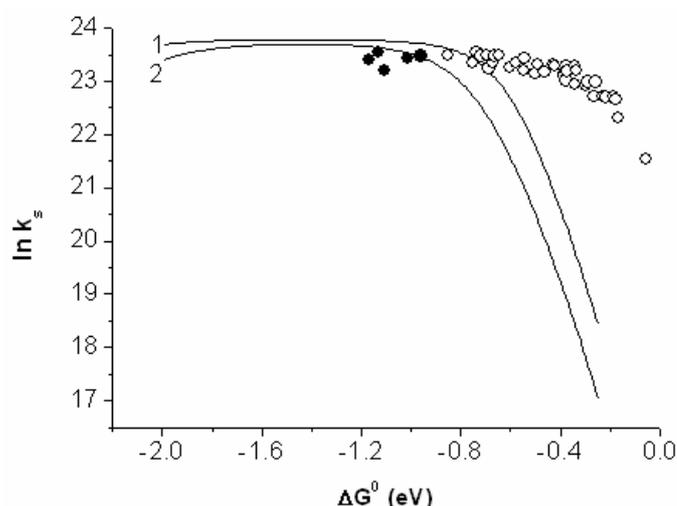
It can be seen that the theoretical calculations agree well with the experimental data for ΔG^0 values in the range of (-0.70eV) – (-1.50eV) but in the normal Marcus region that is for $\Delta G^0 >$ –0.70eV, the experimental values are in a significant disagreement with the theoretically predicted k_S.

For this region, we have used an improved model of Tachiya[6] in which it is considered that an ultrafast electron transfer can take place, at short intermolecular distances, that is between R_{min} and a critical distance, R_c. It is assumed a constant value of k(R), *i.e.*, k(R) equal to the first order rate constant, k_f for R_{min}<R<R_c. The k_f values were obtained by fitting the calculated ks to the experimental ones. In the followings, R_c was taken as 8.5 Å. The values are plotted in Fig. 5.

For R values larger than R_c, the distance dependent rate constant k(R) is calculated using eq. 12 which take into account the contribution of the intramolecular vibration.
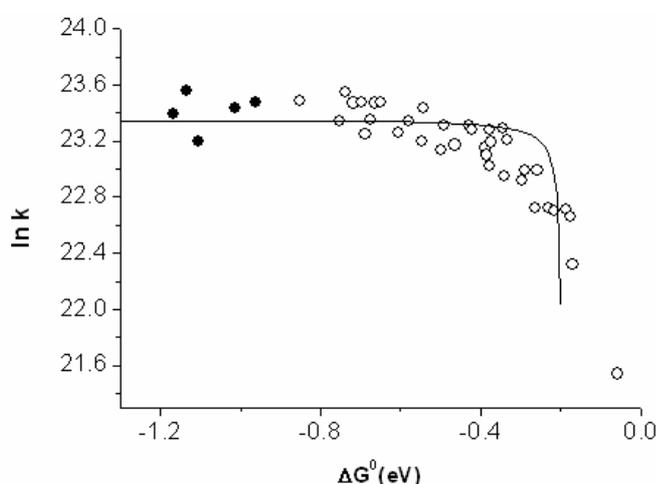
$$k(R) = \frac{4\pi^2}{h} J_0^2 \times exp[-\beta(R - R_0)] \times \frac{1}{\sqrt{4\pi k_B T\lambda}} \times \sum_{m=0}^{\infty} \frac{e^{-S} S^m}{m!} exp\left[-\frac{(\Delta G + \lambda + mh\nu)^2}{4k_B T\lambda}\right] \quad (12)$$

where k_B is Bolzmann's constant, R_0 represents the sum of the acceptor and donor radii, r_D+r_A and R>R_c, ν = 1500cm^{-1}.

For the whole interval, the diffusion-controlled rate constant was taken as 1.34×10^{10} M^{-1} s^{-1}. The results are plotted in Fig. 6. It can be seen a better correlation with the experimental points for the normal Marcus region.

Fig. 5 – Dependence of the k_f values obtained by fitting the calculated k_s to the experimental data on the ΔG^0 values in the range of the normal Marcus region (–0.8) - (-0.3) eV.

Fig. 6 – Best fit to the experimental data obtained by considering the k_f values from the plot in Fig. 5 for R < 8.5 Å and the second order constants for R > 8.5 Å; for the whole R range, $k_D = 1.34 \times 10^{10}$ M^{-1}s^{-1}. (As in Figs. 3 and 4, the filled circles represent our values and the open circles literature data[4] for related coumarin derivatives).

CONCLUSIONS

The applications of the model based on the second order diffusion mediated rate constant of the electron transfer process to the experimental data on the some aromatic amines – coumarin derivatives systems, lead to the following conclusions. As long as only the second order diffusion mediated rate constant was considered, not dependent on the method used to calculate the diffusion constant, a large disagreement between the calculated ks values and the experimental data was obtained for ΔG^0 values in the range (-0.7) – (-0.3) eV, *i.e.,* in the normal Marcus region. As was previously stated by Tachiya, the agreement between the calculated and experimental data was reached only assuming that at short acceptor-donor distances, R< 8.5 Å, a very fast electron transfer occurs with a first order rate obtained by fitting the experimental data. The k_f values obtained, about 10^{11} s^{-1}, show that for the entire ΔG^0 interval, (-0.7) – (-0.3) eV, the electron transfer proce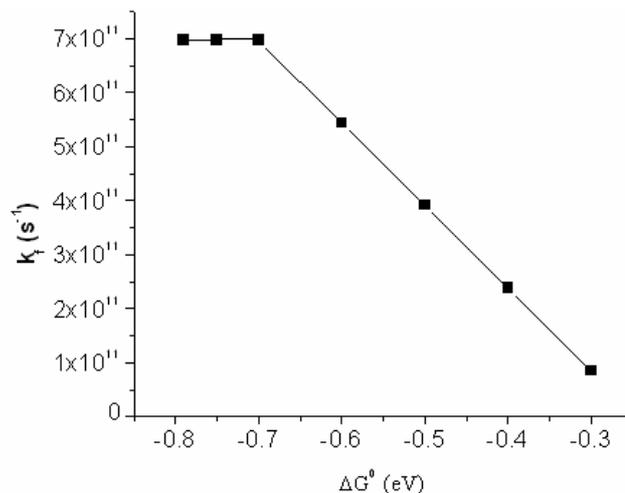ss has also a fast component. At larger R distances a second order diffusion mediated electron transfer must be considered. Concerning the other parameters implied in the model, a better correlation with the experimental data was obtained for $J_0 = 100$ cm^{-1} instead of 50 cm^{-1} used by other authors.[7,8]

REFERENCES

1. C. Tablet and M. Hillebrand, *J. Photochem. Photobiol. A: Chemistry,* **2007**, 189, 73-79.
2. R. A. Marcus, *J. Chem. Phys.,* **1956**, *24,* 966.
3. D. Rehm and A. Weller, *Isr. J. Chem.,* **1970**, *8,* 259.
4. S. Nad and H. Pal, *J. Phys. Chem. A,* **2000,** *104,* 673-680.
5. M. Tachiya and S. Murata, *J. Phys. Chem.,* **1992**, *96,* 8441.
6. S. Iwai, S. Murata and M. Tachiya, *J. Chem. Phys.,* **2001**, *114,* 1312.
7. Xavier Allonas and Patrice Jacques, *Chemical Physics,* **1997**, *215* , 371-378.
8. K. Kikuchi, T. Katagiri, T. Niwa, Y. Takahashi, T. Suzuki, H. Ikeda and T. Miyashi, *Chem. Phys. Lett.,* **1992**, *193,* 156-160.