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Comment on “Exothermic Rate Restrictions in Long-Range Photoinduced Charge Separations”

Gonzalo Angulo,‡ Arnulf Rosspeintner,‡ and Eric Vauthey*‡

‡Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland, and *Physical Chemistry Department, Sciences II University of Geneva, Geneva 1211, Switzerland

Gomes et al. have recently reported in this journal on their experimental observation of exothermic rate restrictions (i.e., Marcus inverted region behavior) in long-range photoinduced charge separation in rigid matrices.†,‡ Although the Marcus inverted region has been well established in charge recombination reactions,³,⁴ its observation for photoinduced bimolecular charge separation in solution (rigid or not) has so far not been reported unambiguously.⁵–¹⁵

The authors performed fluorescence quenching experiments between immobile reactants in glycerol:methanol (9:1) mixtures at 255 K. This medium is supposed to be flexible enough to allow for charge separation and accommodate the reaction products thereof, whereas it efficiently hinders the mutual translational diffusion of the reactants. By doing so, the problem of diffusion limited reactions is notably simplified, because only “static quenching” will be observed. The experimental methods used in these studies were steady-state and nanosecond time-resolved (by means of time correlated single photon counting) fluorescence spectroscopy. The experimental results comprise the change of fluorescence quantum yields and fluorescence time traces at different quencher concentrations spanning a reasonable range of free energy for electron transfer with 8 fluorophore/quencher pairs. These data are analyzed using a model for remote electron transfer with an exponential distance dependence (eq 3 in ref 1), which eventually leads to a fluorescence intensity decay (eq 4 in ref 1) depending on only three parameters: r, the contact distance of the reactants, which the authors estimate using Connolly surfaces; k²₆₇, the rate constant of electron transfer; and β, its distance decay factor (k²₆₇ and β being obtained from the fits to the experiments).

The data analysis consists basically of rescaling the experimental time traces with the fluorescence quantum yields (obtained from the steady-state experiment) and fitting the model to them. Eventually one identical β is obtained for all systems studied and thus the free energy dependence of electron transfer is completely contained in the k²₆₇ values. The so observed “existence of exothermic rate restrictions in photoinduced charge separations in rigid media” is then extensively discussed by the authors.

Unfortunately, however, the authors omitted a self-consistency test on their results. If the time traces, I(t), and thus the kinetics, are well accounted for by the applied model and the obtained parameters, the steady-state quenching experiments (i.e., the change of the fluorescence quantum yield, φ, with quencher concentration, c) also ought to be well reproduced by the time integrals of the model. We may briefly explain this obvious and necessary self-consistency.

\[
\phi = \int_0^\infty \int_0^\infty I(\lambda, t) \, d\lambda \, dt = C \int_0^\infty I(\lambda = \lambda_{\text{em}}, t) \, dt \quad (1)
\]

The first equation merely states that the full kinetics is contained in the steady-state spectrum and that the quantum yield is, except for some scaling factor, C, when only one specific emission wavelength, \( \lambda_{\text{em}} \), is observed instead of the entire emission spectrum, given by the time integral of the fluorescence decay (as long as the effect of the dynamic Stokes shift is negligible). The second equation states that the initial population just after excitation is independent of the quencher concentration. This is true if there is no ground-state complex formation or changes in the properties of the medium that could affect the radiative properties of the fluorophore upon addition of the quencher. Finally, the third equation states that the ratio of steady-state fluorescence intensities at increasing quencher concentration, c, is equal to the ratio of the time integrals of the fluorescence decays at the same concentrations. It can be easily seen that the last equation is simply the outcome of the consequent application of the former two equations.

We tested the self-consistency of the used model and of the obtained parameters by simulating the steady-state results, given in the Supporting Information of ref 2, with the electron transfer parameters given in Table 1 of ref 2. To this end, the same reactivity model (eq 4 from ref 1) was applied to evaluate I(c,t) and eventually integrated numerically to give \( \phi(c) \). The results of this attempt are shown in Figure 1. It can clearly be seen that there is a significant discrepancy between the experimental and simulated data. Irrespective of the inherent reasons for this discrepancy (inappropriateness of the scaling procedure, wrong model, wrong parameters), we are convinced that the appropriateness of the model and the adjoint parameter set ought to be tested on, and should equally well describe, both data sets.⁶–¹⁹

As a consequence, the obtained parameters in general and the electron transfer rate constant, \( k^{0}_{\text{ET}} \), in particular cannot be correct. We thus conclude that the inverted region for this kind of reactions still remains unobserved.

Additionally, we make some further comments:

- It should be noted that the Perrin equation is not correctly written in ref 1 and if used as such will lead to erroneous

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results. The proper equation is given as follows:\(^\text{20}\)

\[
\phi(c = 0) = \exp\left(\frac{4}{3} \pi R_c^3 c\right)
\]

where \(R_c\) is the critical radius (in Å) and \(c\) is the quencher concentration (in Å\(^{-1}\)).

- The critical radii, which, incidentally, are different in the two manuscripts do not reproduce the experimental Perrin plots. In addition, the way they have been extracted is unclear, especially considering that they do not reproduce the Perrin plots.
- In the Correction not only the time-resolved data but also all steady-state data are not the same as the original ones. This fact was neither explained nor pointed out in the Correction.

**Figure 1.** Comparison between experimental (gray line and circles) and simulated (black lines) Perrin plots. The experimental data are calculated on the basis of the linear fits to the Perrin plots shown in the Supporting Information of ref 2 while the simulated data have been calculated using eq 4 and its numeric integral with the parameters given in ref 2.

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**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: eric.vauthey@unige.ch. Phone: +41 22 379 65 37. Fax: +41 22 379 65 18.*

**REFERENCES**


