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Paulo J. S. Gomes, Carlos Serpa,* Rui M. D. Nunes, Luis G. Arnaut, and Sebastião J. Formosinho: Exothermic Rate Restrictions in Long-Range Photoinduced Charge Separations

Page 2778. The first author of the referenced paper has admitted scientific misconduct in the analysis of the kinetic data presented. The data were not fabricated: all the systems reported were effectively measured and all the original (raw) data were properly measured, labeled, and stored. However, the failings involved intentional bias followed by changes in some values calculated for the kinetic decays. We have been able to retrieve all the original experimental data and, because of the importance in confirming the reliability, have repeated some experiments, from which we have verified that they had the expected experimental errors. Examples are illustrated in the Supporting Information. The research worker involved has admitted to have changed experimental points in the single photon counting decays to improve the agreement with the rate constants k_{ET}^0 that best fitted the theoretical predictions shown in Figure 8.

We have repeated the kinetic analysis of the SPC decays with a slightly modified procedure, described below. Coronene exhibited biexponentiality, even in the absence of quencher, and was excluded from the data. Figure 5 of our original paper includes the biased and suspect data and must be replaced by the corrected Figure 5 presented here. The corrected lifetimes and rate constants k_{ET}^0 for photoinduced charge separation for donor−acceptor systems in contact at −18 °C in glycerol/methanol (9:1) are presented in Table 1. Our results now show more scatter, and the values of k_{ET}^0 are 1 order of magnitude smaller than the rate constants of charge recombination in contact radical ion pairs at the same energies, Figure 8. We interpret this difference as resulting from the extrapolation to contact of electron transfer rates between donor and acceptor pairs of random orientation in the glycerol:methanol matrix. Even though there is now more experimental scatter, the main conclusion of our paper, i.e., the existence of exothermic rate restrictions in photoinduced charge separations in rigid media, remains valid. The value of β that best reproduces the experimental data is now in excellent agreement with the value reported by McLendon for glycerol at low temperatures, $\beta = 1.4$ Å^{-1}, ref 40. The value of β reported in the original paper
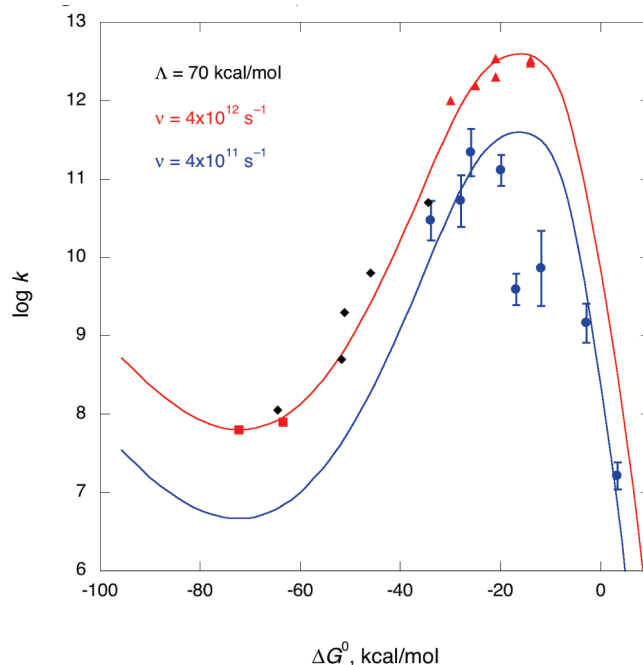
Figure 8. Free-energy dependence of photoinduced charge separation rate constants extrapolated to contact in rigid 9:1 glycerol/methanol matrices (circles) at 255 K. The error bars reflect the range of k_{ET}^0 values that acceptably fit the fluorescence decays at the various quencher concentrations. Charge recombinations in charge-transfer complexes from aromatic hydrocarbons to TCNB adsorbed on porous glass at 77 K (lozenges, ref 64) and to TCNE in acetonitrile (triangles, from data in Table 2) and from aromatic hydrocarbons to FN in CRIP formed in isopropyl ether at 253 K (squares, ref 48) are shown for comparison. The lines represent ISM calculations at 298 K (upper curve) and 255 K (lower curve) with eqs 11 and 12 and tunneling corrections as in ref 48, using the electronic frequencies indicated in the plot, $n^{\ddagger} = 1.8$, $l_r + l_p = 2.7$ Å, $f_r = f_p = 1.15 \times 10^3$ kcal/(mol Å^2), and a total reduced mass for Na and FN of 96.5 amu.

was exaggerated to compensate for the excessive k_{ET}^0 values forced to fit the data.

The revised fitting procedure is a follows. (1) Course graining showed that the values β that gave the best fits to all the decays were in the range 1.3−1.4 Å^{-1}. (2) We imposed $\beta = 1.3$ Å^{-1}
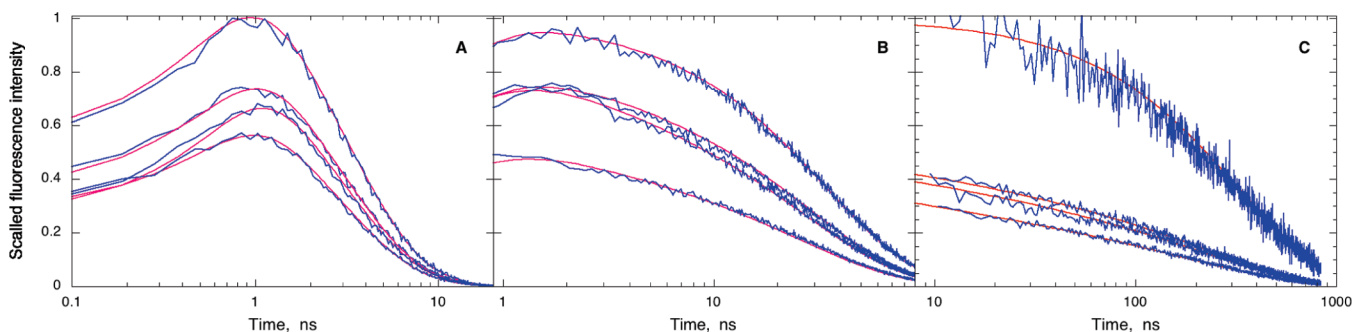
Figure 5. Fluorescence decays in 9:1 glycerol/methanol mixtures at $T = 255$ K and their fittings with eq 6 using $\beta = 1.3$ Å^{-1} and the following rate constants: (A) 1,4-dimethoxybenzene ($\tau = 3.0$ ns) and its quenching by fumaronitrile ([FN] = 0.039, 0.050, and 0.074 M), compared with fits using $k_{ET}^0 = 2 \times 10^{10}$ s^{-1} in all cases; (B) acenaphthene ($\tau = 34$ ns) and its quenching by fumaronitrile ([FN] = 0.099, 0.118, and 0.133 M), compared with fits using $k_{ET}^0 = 1 \times 10^{10}$ s^{-1} (lowest concentration) or 1×10^{11} s^{-1} (intermediate and highest concentrations); (C) pyrene ($\tau = 325$ ns) and its quenching by fumaronitrile ([FN] = 0.123, 0.134, and 0.154 M), compared with fits using $k_{ET}^0 = 1 \times 10^{11}$ s^{-1} (lowest and intermediate concentrations) or 2×10^{11} s^{-1} (highest concentration).

TABLE 1: Reaction Energies, Critical Distances, Lifetimes, and Rate Constants at Contact ($\beta = 1.3$ Å^{-1}) of Photoinduced Charge Separations Measured in Glycerol/Methanol (9:1) Mixtures at -18 °C[a]

system	ΔG^0, kcal/mol	R_c, Å	τ_0, s^{-1}	log k_{ET}^0/s^{-1}
Py + MN	3.3	8.9	325	7.22 ± 0.17
Np + MN	−3.0	15.5	95	9.17 ± 0.25
Bpy + FN	−12	12.1	29	9.87 ± 0.48
Bpe + FN	−17	12.6	109	9.60 ± 0.20
Py + FN	−20	15.6	325	11.12 ± 0.20
Np + FN	−26	13.0	95	11.35 ± 0.30
Ac + FN	−28	9.2	34	10.73 ± 0.33
dmB+ FN	−34	10.1	3.0	10.48 ± 0.25

[a] The uncertainties are the range of the population mean with 90% certainty, using the three highest quencher concentration.

for all the decays. (3) The decays of each fluorophore for the different quencher concentrations were scaled by the relative intensities of their steady-state fluorescence, convoluted with the instrumental response (scatter from a Ludox solution), and the sum of the squared residuals was minimized by changing k_{ET}^0. (4) For long-lived fluorophores such as Py and Np, the channels with substantial convolution with the scatter were ignored, and the decays were scaled at the first point after the scatter became negligible by the relative fluorescence intensities expected from the fitted k_{ET}^0 and steady-state fluorescence intensities.

Supporting Information Available: Fluorescence spectra of aromatic donors in the presence of suppressor in 9:1 glycerol/methanol at -18 °C, for various suppressor concentrations and corresponding Perrin plots. Fluorescence decays in 9:1 glycerol/methanol matrices at -18 °C of the aromatic donors and its quenching by the suppressor. Experimental data fits using monoexponential and nonexponential decay functions. Examples of fits using inadequate parameters and their impact on the quality of fit. This material is available free of charge via the Internet at http://pubs.acs.org.