CHEMPHYSCHEM

Supporting Information

Steady-state emission of pyrene or naphthalene with fumaronitrile in solution *n*-heptane and isopropyl ether yields two bands, the monomer (M) and exciplex (E) bands in all the temperature range studied [30,-50] ^{0}C. The bimolecular nature of the photoinduced charge separation limits the temperature range to the Low Temperature Limit (LTL) in the so-called Stevens-Ban plots, (ln (I_E/I_M) vs. 1/T, where I_E and I_M are respectively the exciplex and monomer fluorescence maximum intensities). From the slope of these plots it is possible to obtain the activation energy for the exciplex formation. The activation energies obtained from these plots, 4.1 kcal mol^{-1} for Py/FN and 2.6 kcal mol^{-1} for Na/FN, are in good agreement with those obtained from time-resolved experiments (see below).

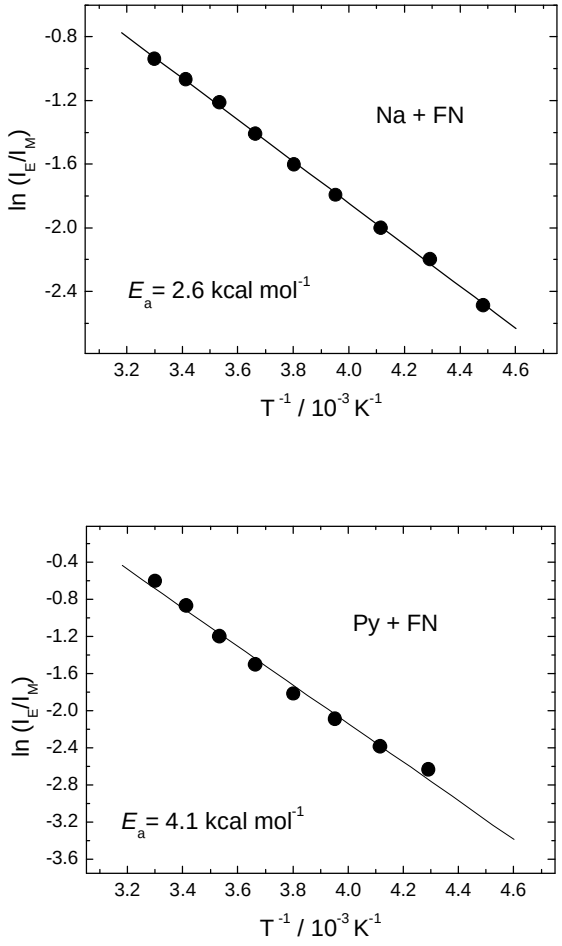

Figure 1. Temperature dependence of the exciplex and monomer relative emission intensities for Na+FN (top) and Py+FN (bottom).

Figure 2 exemplifies the fluorescence decays obtained in isopropyl ether at low temperature. The fluorescence quenching rate constants in *n*-heptane and isopropyl ether, k_q, were obtained by applying the Stern-Volmer equation to steady-state fluorescence, and by Time Correlated Single Photon Counting. The rates obtained by dynamic measurements are the difference between the lifetimes of the fluorophore in the absence (t_0) and in the presence (t_Q) of quencher

$$k_q = \frac{\left(t_Q^{-1} - t_0^{-1}\right)}{[Q]}$$

where [Q] is the concentration of quencher. Steady-state and time-resolved methods gave similar rates. For the milimolar concentrations employed in this study, the absorption by ground-state complexes is negligible and should lead to very short-lived transients. In the time-scales employed, static quenching does not contribute to the observed decays. The absence of static quenching is corroborated by linearity between the reciprocal of the fluorescence lifetimes and the concentration of the quencher.

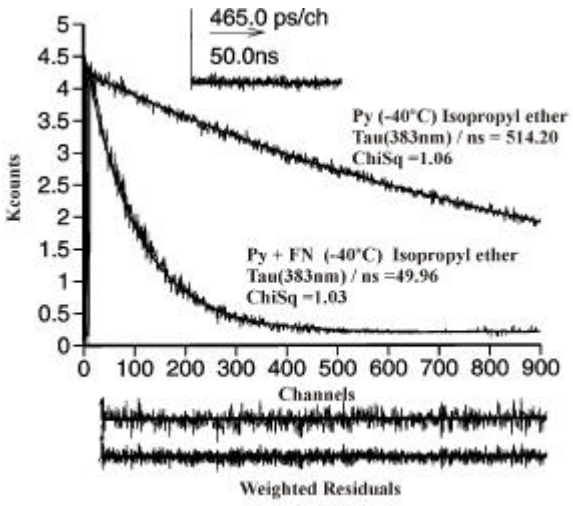

Figure 2. Fluorescence decays for Py and Py/FN ([FN]=5.15x10^{-4} M) in isopropyl ether at -40 °C, and fits obtained for the decays. The insets show the decay times (t_i/ns) and chi-squared values (c^2). Also shown are the weighted residuals for a better judgment of the quality of the fits.

Figure 3 presents the free-energy relationships obtained by time-resolved methods for systems constituted by aromatic hydrocarbons and fumaronitrile. The rates of exciplex formation increase rapidly as $\Delta G°_{exc}$ becomes more negative, and attain the diffusion limit at moderately exothermic reactions. The diffusion plateaus are in good agreement

with the values computed with the equation obtained from the Smoluchowski theory of diffusion controlled reactions:

$$k_{diff} = \frac{8RT}{3h}$$

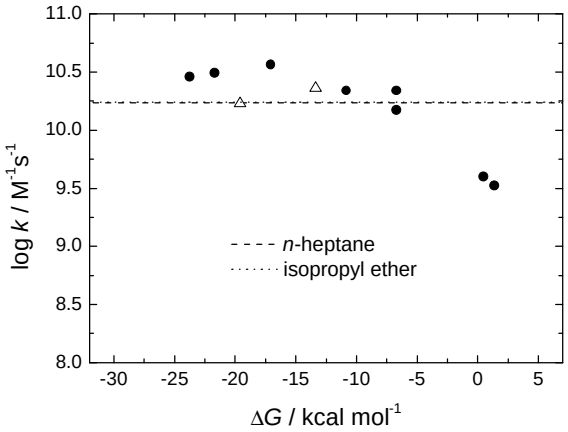

Figure 3. Free-energy relationships in photoinduced charge separation reactions. Benzene with acrylonitrile; 1,4-dicyanobenzene with benzene and toluene; perylene, pyrene, naphthalene, *o*-xylene and *p*-xylene with fumaronitrile. Experimental data: *n*-heptane (circles) and isopropyl ether (triangles). The lines are the diffusion plateaus defined by Eq 7 for *n*-heptane (full line), isopropyl ether (dotted line).

The temperature dependence of the observed quenching rates, $k_q=k_a/[FN]$, together with the reciprocals of t_M, the fluorescence lifetimes of the monomers, are shown in Figure 4. t_M values are weakly temperature dependent. The bimolecular quenching rate constants given in Table 1 and shown in Figure 4 were calculated with concentrations of fumaronitrile corrected for the thermal expansion coefficient of isopropyl ether (a=1.48x10^{-3} K^{-1}).

Table 1. Diffusion rate constant and kinetic data for Na+FN and Py+FN in isopropyl ether. Temperature dependence of isopropyl ether viscosity.

			Na/FN			Py/FN		
T / ^{0}C	h / cP	k_{diff} / 10^{10} M^{-1} s^{-1}	$k_a/10^7$ s^{-1}	[FN]/ 10^{-3} M	$k_q/10^{10}$ M^{-1} s^{-1}	$k_a/10^7$ s^{-1}	[FN]/ 10^{-3} M	$k_q/10^{10}$ M^{-1} s^{-1}
32	0.351	1.93	7.72	3.90	1.98			
31	0.355	1.90				10.6	4.56	2.31
25	0.379	1.74	6.75	3.94	1.71			
17	0.414	1.55				6.10	4.64	1.31
15	0.423	1.51	6.98	4.00	1.75			
5	0.473	1.30	6.12	4.06	1.51			
2.5	0.486	1.26				5.02	4.86	1.03
-10	0.559	1.04	4.69	4.03	1.17	6.75	4.84	1.39
-20	0.624	0.898	4.01	4.20	0.956	3.84	4.91	0.784
-30	0.698	0.772	3.14	4.26	0.738	3.26	4.97	0.656
-40	0.780	0.662				2.02	5.15	0.393
-50	0.871	0.567	2.16	4.38	0.494	1.94	5.22	0.372

The temperature dependence of the quenching rate constant (k_q) follows closely that of the diffusion rate constant calculated with Smoluchowski equation. We calculated k_{diff} with the temperature dependences of the viscosity (h) available in the literature (see Table 1). There is an excellent agreement between k_q and k_{diff}. In fact, the plots in Figure 4 constitute a remarkable example of the adequacy of Smoluchowski equation over an extended range of dielectric properties and temperature.

The temperature dependences of the photoinduced charge separations yield activation energies that cannot be distinguished from those of diffusion. In isopropyl ether we obtained 2.9 kcal mol^{-1} for Py/FN and 2.3 kcal mol^{-1} for Na/FN, whereas in *n*-heptane, where we have a smaller range of temperature, the corresponding values are 4.1 kcal mol^{-1} and 3.6 kcal mol^{-1}, respectively (for T>0 °C).

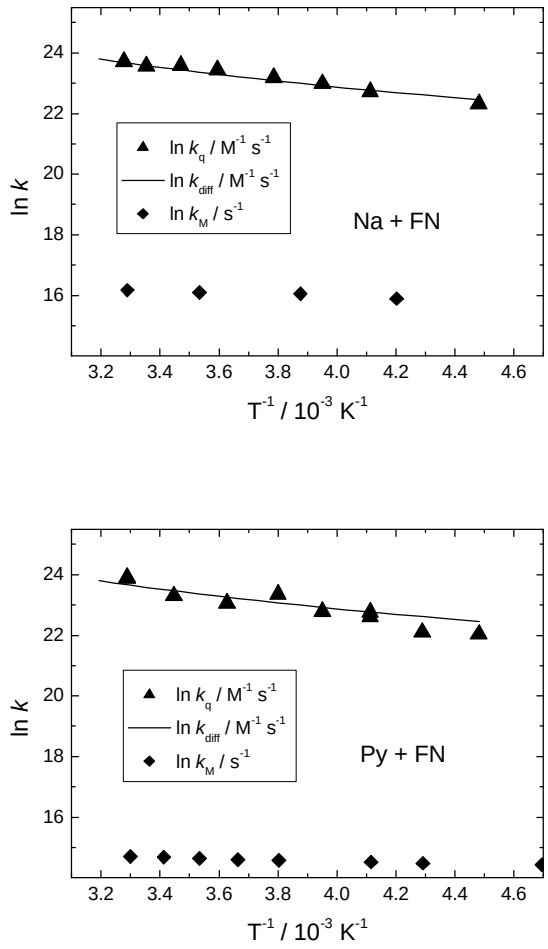

Figure 4. Temperature dependence (Arrhenius plots) of the monomer quenching in isopropyl ether. The reciprocals of the lifetimes of the monomers in the absence of quencher are also shown. The lines are the diffusion rate constants (k_{diff}) calculated with the simplified Smoluchowski equation.