**Assignments for CME-Calc 23 February 2021**

1

Based on the steady state emission intensity, the rate of electron transfer as function of temperature was determined for C60[11]DMA in benzonitrile, in order to experimentally determine the barrier to electron transfer. Try to reproduce these rates of charge separation (approximately) using the Marcus model. The temperature dependence of the di-electric constant can be neglected.

Use Eox = 0.64 V and V = 26.8 cm-1. (You don’t need to use the relative emission intensity or formula (1), data is from JOC 1996).





2

Predict the rates of charge separation for C60[3]TMPD in the other solvents, using the same V as in toluene (V = 100.85 cm-1, see table 3). The rate in toluene was experimentally determined to be 3.33 x 1012 s-1 with femtosecond transient absorption spectroscopy.

Is the trend relative to solvent polarity what you would expect?



3

Calculate the theoretical rate of charge **recombination** for C60[3]TMPD in toluene according to the Classical Marcus model. Use the same electronic coupling as for separation.

(Use Eoo = 2.66 eV to manipulate the driving force, in order to get *G0 (CR) =(-E00 -**G0 (CS)) =* -1.329 eV. Remember that the CDF file is made to look at charge separation, so this is a ‘trick’ to look at charge recombination).

What does this extremely slow rate tell you about the Classical Marcus model? Which model do we need to apply here?? (In which “region” of the Marcus theory is this process occurring? Look at the reorganization energy and the driving force).

(Experimentally the rate of charge recombination was determined to be 2.94 × 1011 s-1)

4

Estimate the rate of electron transfer between pyrene and dimethylaniline in hexane and in acetonitrile:

V = 225 cm-1 (electronic coupling determined with ADF). Take an internal reorganization energy of 0.4 eV.

here is the refractive index of the solvent. is the dielectric constant of the medium. and are the cation and anion radii. is the centre to centre distance between pyrene and dimethylaniline. is the vacuum permittivity and the elementary electron charge.

|  |  |
| --- | --- |
| Radii | Size ( |
|  |  |
|  |  |
|  | 6.50 |

Table 4: The anion, cation radii and the centre to centre distance

|  |  |  |
| --- | --- | --- |
| Solvent |  |  |
| Hexane | 1.37 |  |
| ACN | 1.34 |  |
| Gas | 1.00 | 1.00 |

Table 5: The refractive index and relative permittivity of the solvents at 589.0 nm

The Gibbs free energy consists out of four terms:

1. The energy it costs to oxidize the donor
2. The energy does it costs to reduce the acceptor
3. How much (useable) energy is put in the system by excitation
4. A Coulomb term .

The oxidation potential of the DMA donor, and the reduction potential of the Pyrene acceptor, as well as its singlet state energy in ACN are:

vs SCE in ACN

vs SCE in ACN5

For pyrene6:1

Polar solvents are better at stabilizing charged molecules, making charge separation more favourable in polar solvents.