

My Memorable Moments in Radiation Chemistry

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One of my memorable moments in radiation chemistry came with the findings of pulse radiolysis transient microwave conductivity (TRMC) in conjugated polymers by John Warman and coworkers in Delft. Their amazing observation showed that the (relatively) small mobility of diffusing cations (holes) became large when the holes attached to long, conjugated molecules. This observation also emphasized that pulse radiolysis is uniquely capable to attach electrons or holes to almost any kind of molecule giving it great promise for the future.

Two other special moments came with the demonstration of picosecond pulse radiolysis by John Hunt and coworkers in Toronto. Another was the demonstration in Osaka of subpicosecond pulse radiolysis by Yoshida and coworkers. These two advances let us look at chemical events at astonishingly short times. A third moment was my own, when a signal went missing.

It disappeared! The oscilloscope screen showed, to my disappointment, no trace. Was something wrong with this important sample? This was a pulse radiolysis experiment in the early 1980's on intramolecular electron transfer from biphenyl anion to benzoquinone in the compound BSA (Fig. 1). I had seen that the electron transfer occurred in a few ns in moderately-polar MTHF as a solvent. That 20 times *slower* than the rate for a similar compound having an acceptor group with lower electron affinity, confirming the "inverted region" predicted by the Marcus theory. Now to the same molecule was dissolved in non-polar isooctane to test a 2nd prediction of the Marcus theory that the inverted effect would be larger (still slower rates) in a non-polar medium. But the signal was missing!

I pulled out the polaroid picture— yes that's how we made measurements in those days! I could see that the trace was off-scale, but not completely: a small piece of it crossed the upper right corner. A lower gain on the

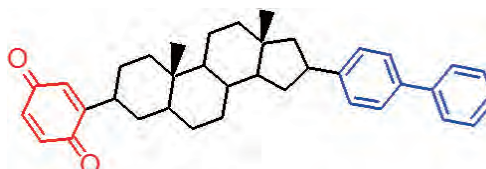


Figure 1. The compound BSA having biphenyl and benzoquinone attached to a rigid steroid spacer.

scope input amplifier revealed that the absorption transient was much larger and decayed almost hundred times more slowly than in MTHF: the intramolecular electron transfer was far slower in the non-polar medium. The very slow electron transfer meant that growth of biphenyl anions was not compensated by fast decay thus driving the transient absorption off-scale. For me this was a stunning confirmation of Marcus's prediction about the effect of polarity in the inverted region.

Radiation Chemistry methods continue to be an outstanding tool to examine electron transfer in non-polar media. While the inverted region is usually not seen in bimolecular electron transfer, as first shown by Rehm and Weller, we suspect that the main reason is the diffusion-controlled limit. For bimolecular reactions of electrons in some non-polar liquids radiation chemistry methods have found that the electrons have mobilities up to 100 cm²/Vs. Dick Holroyd in our laboratory found that reactions of those high-mobility electrons can become free of the diffusion-controlled limit. Further, the free energy changes for those reactions can be adjusted continuously over an almost 300 meV range using methods found by Dick and his collaborators. We applied this method to find a small inverted region and evidence for inverted suppression of one reaction by a factor of at least 10⁵ (Holroyd and coworkers, *J. Phys. Chem. B*, 118 (2014) 2164). These studies have great potential and are possible only with radiation chemistry.

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