# DRIVING FORCE DEPENDENCE OF ELECTRON TRANSFER OXIDATION OF FULLERENES

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The most important prediction of the Marcus theory of electron transfer (ET) is that the ET rate decreases as the ET driving force ($-\Delta G^0_{ET}$) increases for strongly exergonic region ($-\Delta G^0_{ET} < \lambda$ which is the energy required to structurally reorganize the donor, acceptor and their solvation spheres upon ET: reorganization energy).[1] This is called Marcus inverted region, which has now been well-established in a number of systems with donor/acceptor at fixed distances after long controversy.[2] However, definitive evidence for the inverted region has almost been nonexistent for bimolecular ET reactions. These bimolecular reactions normally follow the Rehm-Weller behavior such that the ET rate increases with an increase in driving force, reaches a diffusion-limit and remains unchanged no matter how exergonic the ET becomes.[3]

There have been a few reports on observations of the inverted region, but the claim was questioned later.[4] The inverted region should be discerned for those ET reactions with small $\lambda$ and large driving force. These criteria are present for bimolecular ET reactions involving fullerenes, which may have small reorganization energies due to their highly delocalized $\pi$ electron systems. In fact, pulse-radiolytic studies, focusing on *inter*molecular charge-shift dynamics between fullerenes and a series of radiolytically generated arene $\pi$-radical cations, revealed a tendency of an decrease in the ET rate as the difference in the respective arenes' and fullerenes' ionization potentials increases.[5] This seems to be the most promising case for observation of the Marcus inverted region for bimolecular ET reactions. However, definitive evidence for the inverted region has yet to be reported using the $-\Delta G^0_{ET}$ values, determined experimentally from the redox potentials in solution instead of using the values estimated from the difference in their ionization potentials. This is reported herein and the $\lambda$ values of ET reactions between fullerenes and arene $\pi$-radical cations are determined based on the parabolic dependence of the ET rates on $-\Delta G^0_{ET}$.

The one-electron oxidation potentials of arenes, which correspond to the one-electron reduction potentials of arene $\pi$ radical cations in dichloromethane were determined using the second hamonic ac voltammetry. These values together with the known values of fullerenes ($C_{76}$ and $C_{78}$) employed in this study provide the firm experimental values of the driving force of electron transfer between fullerenes and arene $\pi$ radical cations.

The substantially reduced ionization potentials of $C_{76}$ ($D_2$) ($IP$ = 7.1 eV) and $C_{78}$ ($C_{2v'}$) ($IP$ = 7.05 eV) relative to $C_{60}$ ($I_h$) ($IP$ = 7.59 eV) are much more beneficial for following the envisaged bimolecular ET processes, which now becomes possible with a significantly increased number of suitable electron accepting substrates using arene $\pi$ radical cations. $C_{76}$ (see Figure 1) reveals a striking parabolic dependence, that is, a decrease of the rate constants with increasing the driving force. Most interestingly, the pronounced decrease towards the highly exothermic region represents the first definitive confirmation of the existence of the Marcus *inverted* region in a truly bimolecular electron transfer. The ratio between the maximum rate and the rate at the high exothermic end (mesitylene) in our set of experiments is 13. By fitting these experiments with the Marcus equation for bimolecular ET reactions,[1] an experimental value of *ca.* 0.35 eV was deduced for the total reorganization energy of $C_{76}$ in dichloromethane. Similar results were obtained for $C_{78}$. The bimolecular ET reactions of $C_{60}$ were also examined and the $\lambda$ values of these fullerenes are compared.

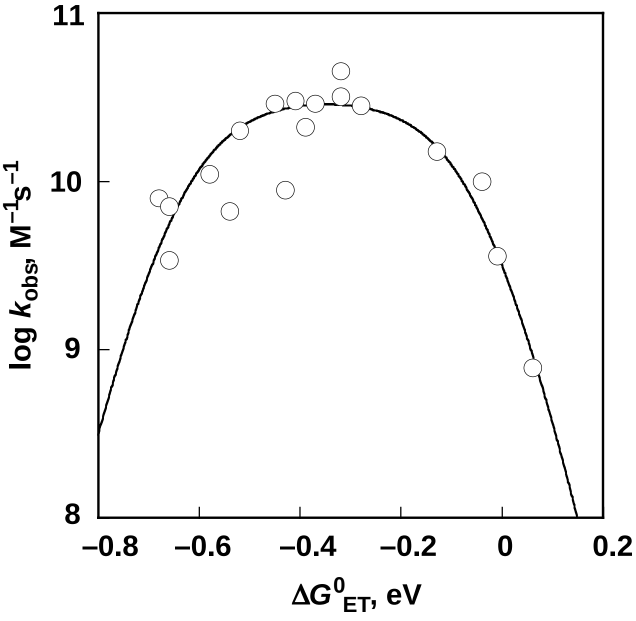

**Figure 1.** Plot of log $k_{obs}$ vs $\Delta G^0_{ET}$ for electron transfer from $C_{76}$ to arene $\pi$ radical cations in dichlomethane.

## References

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