Sorting Out the Effects of Electron-Transfer Distance, the Electrical Double Layer and the Inner Reorganization Energy in Heterogeneous Electron-Transfer Reactions of Organic Compounds

Dennis H. Evans
Department of Chemistry and Biochemistry
University of Delaware
Newark, Delaware 19716 (USA)

The most easily studied electron-transfer reactions of neutral organic compounds are those that occur at relatively mild potentials, *i.e.*, potentials that are not too close to the cathodic or andodic potential limit. Most such compounds feature delocalization of charge in the radical ions (lowering the outer reorganization energy) and quite minor changes in structure (lowering the inner reorganization energy). Consequently, the electron-transfer reactions are quite facile and it is experimentally difficult to obtain reliable values of the electron-transfer rate constants, k_s, which are large.

One of the few classes of molecules that are reduced at potentials that are well removed from the cathodic potential limit and that feature rather small values of k_s, are the nitroalkanes. It was noted over three decades ago (1) that k_s values for nitroalkanes were unusually small and this was interpreted as being due to localization of charge in the radical anion in the three atoms of the nitro group thus increasing the outer reorganization energy.

Subsequently, it was also found that the values of k_s were also highly dependent on the size of the cation of the supporting electrolyte, decreasing about two orders of magnitude on going from $(C_2H_5)_4N^+$ to $(n\text{-}C_7H_{15})_4N^+$. It turned out that plots of $\ln(k_s)$ *vs.* the diameter of the cation were linear with slopes corresponding to normal values of the attenuation coefficient, β, in $k_s = A\exp(-\beta x)$ where x is the distance of closest approach of reactant to the electrode surface as governed by the layer of R_4N^+ on the electrode that is probably present at the rather negative potentials required for the electrode reaction. Hence, the effect of cation size was interpreted as an effect of <u>electron-transfer distance</u>. Similar effects have been seen by a number of workers for a variety of systems, including nitroarom-atics.

In essence, this is a <u>double layer effect</u>, as it arises from the structure of the electrical double layer at quite negative potentials and in the presence of large, adsorbable tetralkylammonium cations. Another trend was not, however, explained by this model. With any given R_4N^+ in the electrolyte, the values of k_s decreased about a factor of ten on going from R' = Me to R' = *tert*-Bu in $R'NO_2$. Calculations show that this is not likely to be due to changes in inner or outer reorganization energies. Interestingly, the effect can also be interpreted as an effect of <u>electron-transfer distance</u> if it is considered that the nitroalkanes with larger alkyl groups will, on the average, be unable to approach the electrode as closely as can those with small alkyl groups. This effect, dubbed the "*tert*-butyl effect", has been seen with other systems as well.

Another double layer effect, the classical Frumkin correction, has not yet been mentioned. This effect is attributed to the more negative potential that exists at the reaction site (often assumed to be the outer-Helmholtz plane) as the potential of the electrode is made more negative. Studies of a variety of compounds show that there is a gentle suppression of k_s as couples with more and more negative $E°$ are studied, consistent with a Frumkin correction. However, the nitroalkanes fall distinctly below this trend.

So, another explanation is needed for the low values of k_s found for the nitroalkanes, irrespective of the size of the alkyl group. A hint about the source of this factor can be found in early molecular orbital calculations that show that there should be significant pyramidalization at nitrogen in going from the planar neutral nitroalkane to the radical anion. Later high-level DFT calculations have confirmed this structural change and indicate that there is a significant <u>inner reorganization energy</u> for the process. This is perhaps not surprising as the reduction essentially involves only the three atoms of the nitro group and the introduction of an electron might be expected to induce a structural change in contrast to aromatic systems where the added electron enters a π system inducing minor structural changes.

The calculated contributions of this structural change to the values of k_s indicate that it is roughly independent of the size of the alkyl group and its magnitude is approximately correct to explain the anomalously small values of k_s that are observed for the nitroalkanes.

Interestingly, this general interpretation may also be relevant to the electron-transfer reactions of nitroaromatics. A recent evaluation of the k_s-values of five nirobenzenes (2-methyl-, 2,6-dimethyl, 2,4,6-trimethyl, 2,3,5,6-tetramethyl- and pentamethylnitro-benzene) has shown that the values of k_s decrease as the number of methyl groups in the compound is increased. The classical explanation is, once again, that the electron-donating alkyl groups force more of the charge onto the nitro group and increase the outer reorganization energy. This is likely to be a contributing effect. However, and somewhat surprisingly, high-level calculations show that the radical anion of, for example, pentamethylnitro-benzene shows significant pyramidalization at nitrogen, just as do the nitroalkanes. That is, as the electron-donating groups force more charge (and spin, presumably) into the nitro group, that group acts more and more like the nitro group of a nitroalkane. Thus, it is suggested that there is a significant <u>inner reorganization energy</u> contribution to the activation energy for reduction of polymethyl nitrobenzenes.

Reactant size effects (discussed above) are probably not prevalent here as 2,4,6-tri(*tert*.-butyl)nitrobenzene has a k_s only slightly smaller than 2,4,6-trimethylnitrobenzene.

The intimate interleaving of the effects of <u>electron-transfer distance</u>, <u>electrical double layer</u>, and <u>inner reorganization energy</u> causes considerable difficulty in separating them quantitatively. Nevertheless, the present analysis provides a qualitative picture of the factors that influence these interesting electron-transfer reactions.

---

1. Because of space limitations, literature citations will not be given here. The full paper will discuss the results of the many workers who have contributed to our understanding of these aspects of electron-transfer kinetics or organic compounds.