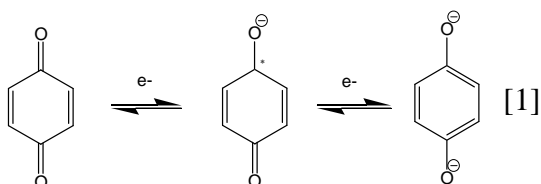


Quinone Electrochemical Mysteries: Thick Cyclic Voltammograms and Tiny Redox Waves

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Quinones are well-known to undergo two reversible reductions at glassy carbon electrodes in aprotic solvents, first to a radical anion and then to a dianion, eq 1. Despite 50+ years of voltammetric investigation of this chemistry, two unusual features of quinone voltammetry—that the second redox wave is smaller than the first, and that the area between the two waves is thicker than CV simulations say it should be—was typically ignored until Gupta and Linschitz made note of the difference of redox waves in 1997.¹ The current explanation for the unequal wave heights, advanced by Macías-Ruvalcaba and Evans in 2010,² is that some of the radical anion is trapped in the form of a pi dimer in solution. Macías-Ruvalcaba and Evans hypothesize that this dimer can be reduced at the same potential as the monomer radical anion, but only by 1 e⁻ per dimer, resulting in smaller current than expected. There currently is no explanation in the literature for the thickness between the two waves.



In this study, concentration dependence on the CVs of differently substituted quinones showed that radical dimerization cannot be a general explanation for the small second redox wave. It has been observed with the quinone vitamin K that under extremely dry conditions in methylene chloride that the second redox wave is totally irreversible, however the height of the reduction peak is correct for a 1e⁻ wave. More importantly, addition of water increases the reversibility while sacrificing the size of the wave. These results suggest that the quinone dianion, when not H-bonded, is highly reactive; they also suggest that water decreases the reduction current to less than one electron per

radical anion. Perhaps this is due to some aggregate formed by water, radical anions, and dianions, but the specifics are not clear at present.

In some cases the thickness between the waves appears as its own reversible wave. Addition of phenols to a quinone solution produces a reversible wave at the same potential due to hydrogen bonding to the radical anion. The McCreery lab showed that oxide content of the surface of glassy carbon can change its chemistry through the presence of functional groups such as phenols.³ In low concentration duroquinone studies, different surface treatments show that with higher oxide content a new wave grows in that is at the same potential as the wave seen in a 1:1 addition of naphthol to the quinone redox system. This indicates that the odd thickness in quinone CV's may be due to hydrogen bonding of the quinones to phenolic groups on the glassy carbon surface.

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