

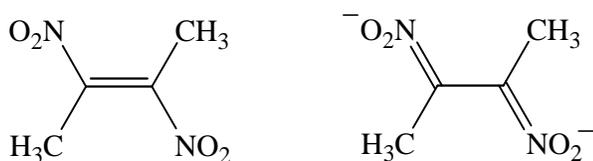
# REDUCTION OF *trans*-2,3-DINITRO-2-BUTENE. A TWO-ELECTRON REACTION WITH INVERSION OF STANDARD POTENTIALS

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Many organic compounds can be electrochemically oxidized or reduced in a series of steps and it is normally found that removal or insertion of electrons becomes progressively more difficult on moving from one step to the next. However, there are examples where, for example, a two-electron reduction occurs with the standard potential for the second step being more positive than that of the first. In other words, insertion of the second electron occurs more readily than the first. Such behavior has been called potential inversion.<sup>1</sup>

In most cases such potential inversions are caused by structural changes that usually follow the introduction of the first electron though the details of the timing of electron transfer and structural change are often obscure. It is also common that the structural change relieves steric crowding in the molecule so the driving force is understandable. It was therefore quite surprising to find an early report of apparent potential inversion in the reduction of *trans*-2,3-dimethyl-2-butene<sup>2</sup> because there are no obvious steric factors influencing the structure of the neutral, radical anion or dianion (see below).



Initial studies of the reduction of *trans*-2,3-dimethyl-2-butene in acetonitrile revealed some surprises. A two-electron reduction was observed but the dianion underwent a rapid followup reaction, one of the products of which was nitrite. We suppose that a double cleavage reaction occurs giving 2-butene and two nitrite ions.

When conditions more closely resembling those of the first report were used, *viz.*, 80% aqueous carbonate/bicarbonate buffer, 20% acetonitrile, the dianion was stable on the

voltammetric time scale but the reactions were electrochemically irreversible when a glassy carbon electrode was used, the peak separation being about 0.8 V at 0.2 V/s. When a mercury drop electrode was used, the peak separation decreased to 42 mV under the same conditions. The electron-transfer kinetics are unusually sensitive to the nature of the working electrode.

All additional measurements were made with a hanging mercury drop electrode and with a mixed solvent of 83% acetonitrile, 17% water with 0.10 M Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte. Under these conditions the dianion is stable on the voltammetric time scale. The earlier report demonstrated that protonation does not occur but our results show that there is considerable stabilization of the dianion and radical anion by hydration as demonstrated by a positive shift of the overall two-electron standard potential of about 0.4 V on going from pure acetonitrile to the mixed solvent. We suppose that the hydration is also responsible for the smaller decay rate of the dianion in the mixed solvent.

Cyclic voltammograms at mercury in the mixed solvent show clear evidence of potential inversion. The data are well accounted for by digital simulations using  $E^{\circ}_1 = -0.600$  V and  $E^{\circ}_2 = -0.515$  V *vs.* the standard potential of the ferrocene/ferrocenium couple.  $E^{\circ}_1$  is the standard potential for the neutral/radical anion couple and  $E^{\circ}_2$  is the potential for the radical anion/dianion couple. Thus, the extent of potential inversion is 85 mV.

The cause of the inversion may be related to structural changes that are predicted to accompany or follow electron transfer. Semi-empirical molecular orbital calculations (AM1) indicate that the planar neutral (N-C-C-N torsional angle =  $\theta = 180^\circ$ ) twists about the central C-C bond in the radical anion ( $\theta = 158^\circ$ ) and even more in the dianion ( $\theta = 125^\circ$ ). These changes are associated with a lowering of the LUMO energy, a factor that has been previously shown to underlie potential inversion. Twisting about the central bond clearly does not relieve steric crowding. The origins for this structural change are purely electronic.

## References

1. Evans, D. H.; Hu, K. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3983.
2. Armand, J.; Convert, O. *Collect. Czech. Chem. Commun.* **1971**, *36*, 351.