

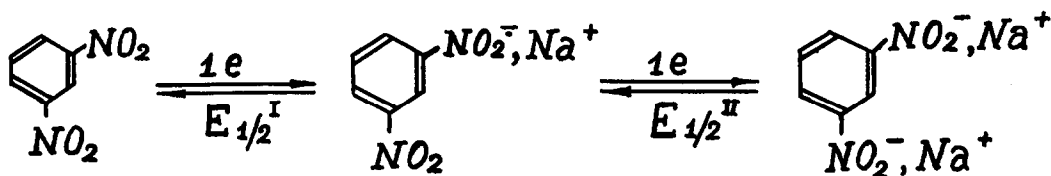
CONVERSION OF THE AROMATIC NITRO GROUP INTO  
A DONATING SUBSTITUENT BY ELECTRON CAPTURE

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The one-electron reduction of aromatic nitro compounds yields anion-radicals characterized by effective electron localisation on the nitro group<sup>1</sup>. However, the nitro group is known to be a many-electron acceptor. For instance, the nitrobenzene anion-radical takes on three more electrons, on the dropping mercury electrode in dimethylformamide (DMF)<sup>2</sup>. Since many important reactions of aromatic nitro compounds are believed to proceed through the stage of anion-radical formation<sup>3</sup>, it is essential to know whether the nitro group retains its acceptor properties after the capture of one electron.

In order to shed light on this question we studied the polarographic reduction of a series of substituted nitrobenzenes in 0.1M NaClO<sub>4</sub> in DMF. In all cases, the process begins with the reversible transfer of one electron. For m-dinitrobenzene both the first and the second waves are one-electron and reversible, as revealed by DC polarography and cyclic voltammetry.



The half-wave potentials ( $E_{1/2}$ ) depend linearly on the  $\sigma^\circ$  constants expressing the inductive effect of the substituted phenyl ring on the reaction center<sup>4</sup> (Table). The data for both meta and para substituted nitrobenzenes fall on the same straight line expressed by equation  $E_{1/2} = -1.115 + 0.456 \sigma_{m,p}^\circ$  with a correlation coefficient  $r = 0.972$ , number of points  $n = 13$  and a standard deviation ( $S_x$ ) for  $\sigma_{m,p}^\circ$  of  $\pm 0.07$ .

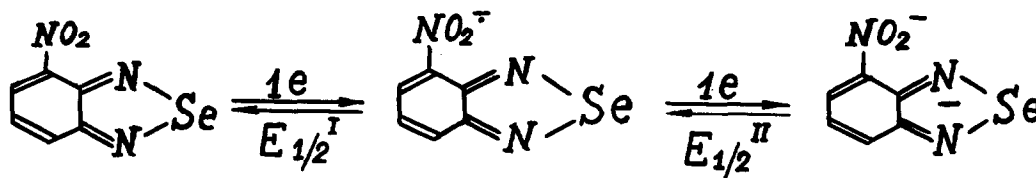
Table.  $E_{1/2}^I$  of substituted nitrobenzene (versus s.c.e.)

Group	$-E_{1/2}, V$	Group	$-E_{1/2}, V$
m - NO <sub>2</sub>	0.86	p - NO <sub>2</sub>	0.63
m - Cl	0.97	p - I	1.00
m - COOCH <sub>3</sub>	0.98	p - Cl	1.01
m - OH	1.08	p - CH <sub>3</sub>	1.11
m - NH <sub>2</sub>	1.18	p - OH	1.15
m - I	0.99	p - OCH <sub>3</sub>	1.20
		p - NH <sub>2</sub>	1.31

The effect of the m-NO<sub>2</sub><sup>-</sup> -substituent is, of course, the most informative for our purpose. This group cannot be in conjugation with the reaction center<sup>5</sup> so that the conditions are favorable for the manifestation of any possible acceptor effect. Thus, the methoxy group which acts as donor in the ortho and para positions of the benzene ring acts as acceptor in the meta position<sup>4</sup>. Regrettably, there are no reported  $\sigma_{m-NO_2}^\circ$  values. In order to evaluate this constant we postulated that since all the  $\sigma^\circ$  values for both meta and para substituents fall on the same straight line, the  $\sigma_{m-NO_2}^\circ$  value should also fall on this line. Hence, plotting the point for the second half-wave potential ( $E_{1/2}^{II} = -1.192 V$ ) of the m-dinitrobenzene on the line, we find the  $\sigma^\circ$  value for the m-NO<sub>2</sub><sup>-</sup> -substituent to be -0.17. If the level of significance is taken as 0.05, than for  $n = 13$ , Student's criterium will be 2.2 and the interval of confidence of the  $\sigma_{m-NO_2}^\circ$  constant will be from -0.02 to -0.32. Hence  $\sigma_{m-NO_2}^\circ$  is negative over the entire interval of confidence. It should be recalled that for the nitro group  $\sigma_{m-NO_2}^\circ = + 0.70^4$ . The change in the sign of  $\sigma^\circ$  means that the nitro group, which is a strong electron-accepting substituent, becomes an electron donor after the capture of one electron. The result which may at first sight be somewhat surprising. However, it can be explained by the fact that under the experimental conditions (when m-dinitrobenzene is converted into the sodium salt of the anion-radical), there is a strongly non-equivalent distribution of the captured electron between the two nitro groups. In fact, ESR data have shown that for this salt the coupling constant is 9.0 G

for one nitrogen atom and only 0.2 G for the other<sup>6</sup>.

Our conclusion is supported also by data from another series of entirely different compounds, namely 3- and 4-substituted benz-(1,2-c)-(1,2,5)-selenadiazoles. The  $\sigma_{m-\text{NO}_2}^\circ$  constant was calculated in the same manner from the half-wave potentials of the reversible one-electron reduction in DMF with 0.05M  $\text{Et}_4\text{NBr}$  as supporting electrolyte. In the case of the nitro derivative the first two stages of the polarographic electron transfer have been shown<sup>7</sup> to follow the scheme:



The  $E_{1/2}^-$   $\sigma_{m,p}^\circ$  dependence for the selenadiazoles obeys the equation  $E_{1/2}^- = -1.332 + 0.551 \sigma_{m,p}^\circ$  ( $n = 10$ ,  $r = 0.990$ ,  $S_x = 0.04$ ). From this we obtain  $\sigma_{m-\text{NO}_2}^\circ = -0.16$ . If the level of significance is taken as 0.05, Student's criterion will be 2.3 and the interval of confidence for  $\sigma_{m-\text{NO}_2}^\circ$  will be from -0.07 to -0.25. Hence here also the  $\sigma_{m-\text{NO}_2}^\circ$  constant is negative over the whole confidence interval.

The numerical values for this constant are the same in the two reaction series considered. Consequently, this constant is most probably of a general nature and should be applicable to widely differing nitroaromatic anion-radicals.

#### References

1. D.Geske, J.Ragle, M.Bambenek, A.Balch, *J.Am.Chem.Soc.*, **86**, 990 (1964).
2. W.Kemula, R.Sioda, *Bull.Acad.polon.sci.Ser.chim.*, **10**, 107 (1962).
3. N.Holy, J.Marcum, *Angew.Chem.*, **83**, 132 (1971).
4. P.Zuman, *Substituent Effects in Organic Polarography*, Plenum Press, New York, 1967, Chapt. 3.
5. C.Fyfe, A.Albagli, R.Steward, *Can.J.Chem.*, **48**, 3721 (1970).
6. R.Ward, *J.Chem.Phys.*, **36**, 1405 (1962).
7. Z.V.Todres, V.Sh.Tsvenishvili, S.I.Zhdanov, D.N.Kursanov, *Dokl.Akad.Nauk SSSR*, **181**, 906 (1968).