Sodium Borohydride Reduction of Aromatic Nitro-compounds

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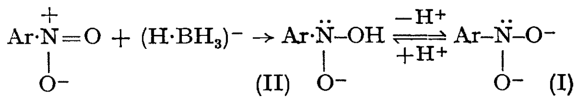
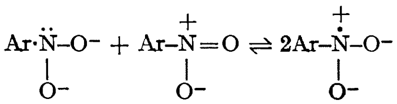
Summary Aromatic nitro-compounds in aqueous or aqueous–alcoholic alkali are reduced by sodium borohydride to their radical-anions, $(\mathrm{ArNO_2}\cdot)^-$.

CONTRARY to general belief[1] we have found that aromatic nitro-compounds are reduced to some extent by sodium borohydride in aqueous or aqueous–alcoholic alkali at room temperature. Nitrogen-flushed solutions of nitrobenzene, *p*-nitrotoluene, *p*-nitroanisole, *p*-fluoro- or *p*-chloro-nitrobenzene in aqueous methanolic sodium hydroxide or of aqueous sodium *p*-nitrobenzoate or sodium *p*-nitrophenolate in water at pH $\geqslant 10$ when treated with sodium borohydride have been found to exhibit the e.s.r. spectra of their corresponding radical-anions, $(\mathrm{ArNO_2}\cdot)^-$. In static mixtures these spectra soon develop and within 0·5 hr. reach a maximum intensity, corresponding to from 0·01 to 1% of the nitro-compound taken, which is then maintained for several hours.

Since there is no reason to suppose that sodium borohydride acts other than by hydride transfer we suggest that the radical formation is a further example of the $\pi^{2-} + \pi \leftrightharpoons 2(\pi\cdot)^-$ equilibrium which Russell, Jansen, and Strom[2] have shown to be a general route for radical-anion formation (equations 1, 2). If this mechanism is accepted then the reason why carbonyl compounds $\mathrm{R_2CO}$ are reduced by sodium borohydride in preference to nitro-compounds in spite of the unfavourable order of their redox potentials[3] becomes evident. Both the ions (I) and (II) have a stable site, on nitrogen, for an unshared electron pair but the anions, $\mathrm{R_2C^-{-}O^-}$ and $\mathrm{R_2C^-{-}OH}$, are carbanions which would protonate immediately and irreversibly, thus driving forward any reduction. When this complete protonation does not occur, *e.g.* with quinones, and a di-anion can exist, then radical-anions detectable by e.s.r. are formed by borohydride reduction. This was verified by using sodium anthracene-β-sulphonate in aqueous methanol. Again if the reacting solutions are not nitrogen flushed then $(\mathrm{ArNO_2}\cdot)^-$ radicals would not accumulate since they are immediately oxidised by free oxygen. This procedure is seldom adopted for sodium borohydride reductions.



$$\underset{\mathrm{O^-}}{\mathrm{Ar{\cdot}\overset{+}{N}{=}O}} + (\mathrm{H{\cdot}BH_3})^- \rightarrow \underset{\mathrm{(II)\quad O^-}}{\mathrm{Ar{\cdot}\ddot{N}{-}OH}} \underset{+\mathrm{H}^+}{\overset{-\mathrm{H}^+}{\rightleftharpoons}} \underset{\mathrm{O^-\quad (I)}}{\mathrm{Ar{-}\ddot{N}{-}O^-}} \qquad (1)$$



$$\underset{\mathrm{O^-}}{\mathrm{Ar{\cdot}\ddot{N}{-}O^-}} + \underset{\mathrm{O^-}}{\mathrm{Ar{-}\overset{+}{N}{=}O}} \rightleftharpoons 2\underset{\mathrm{O^-}}{\mathrm{Ar{-}\overset{+}{\dot{N}}{-}O^-}} \qquad (2)$$

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[1] See for example H. C. Brown, "Hydroboration," Benjamin, New York, 1962, ch. 17.

[2] G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Amer. Chem. Soc.*, **1964, 86**, 1807; 1962, **84**, 4155.

[3] J. M. Fritsch, T. P. Layloff, and R. N. Adams, *J. Amer. Chem. Soc.*, 1965, **87**, 1724.