# Hydrogen Isotope Exchange between Nitrobenzene and Sodium Borohydride

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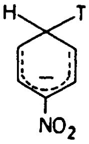
*Summary* Reaction between tritium-labelled sodium borohydride and nitrobenzene in dimethyl sulphoxide solution at 25 °C leads slowly to tritium incorporation into nitrobenzene, with the implication of reversible hydride (tritide) transfer between the reactants.

THE reduction of organic compounds by hydride-donor reagents, typified by sodium borohydride, is usually thought to proceed by a rate-controlling hydride transfer and succeeding rapid steps.[1] An alternative, hitherto unreported and largely ignored, reaction path might involve a reversible hydride transfer to the substrate with a subsequent rate-limiting step. These two mechanisms, both of which may be realisable under appropriate conditions, are the hydride analogues of two of the most familiar mechanisms of acid catalysis, *viz.* those in which proton transfer is respectively rate-limiting or a pre-equilibrium.[2]

We now report what is thought to be the first recognised case of a reversible hydride transfer to an organic compound. Tritium-labelled sodium borohydride (activity $A_0 = ca.$ 0·01 Ci per mol/4) prepared by adaptation of a published synthesis[3] of the deuteriated analogue) was found to react with nitrobenzene in dry dimethyl sulphoxide solution to produce labelled nitrobenzene. At 25 °C the second-order rate constant of the exchange reaction:

$$k = (A/A_0)_{t \rightarrow 0}/t[\mathrm{BH_4^-}]$$

(where $A$ is the tritium activity of nitrobenzene per mol after time $t$) is *ca.* $5{\cdot}8 \times 10^{-7}\ \mathrm{s^{-1}\ mol^{-1}\ dm^{3}}$. Under these experimental conditions there is no complication from radiation-induced exchange processes,[4] nor is there detectable reduction of the nitro-group[5] or of the benzene ring[6] or displacement of the nitro-group.[7] The only plausible exchange mechanism is an associative one with formation of the nitrocyclohexadienyl anion [(I) or its positional isomers] as an intermediate. This intermediate must lose H$^-$ to revert to nitrobenzene, but it has not yet been established whether BH$_4^-$ is regenerated in the same step.


(I)

The tetramethylammonium salt of the trinitro-analogue of (I) (*i.e.* the hydride Meisenheimer complex of 1,3,5-trinitrobenzene) can be isolated as a stable compound.[8]

The observation of aromatic hydrogen exchange *via* hydride transfer and intermediate formation of (I) completes the trio of aromatic exchange reactions of the general pattern involving cyclohexadienyl intermediates. The other two are acid-catalysed exchange,[9] where cyclohexadienyl cations are the intermediate species, and the free-radical path in which cyclohexadienyl radicals are formed and which can be realised as a radiation-induced process.[4]

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