Isotope Exchange in Borohydride Reductions

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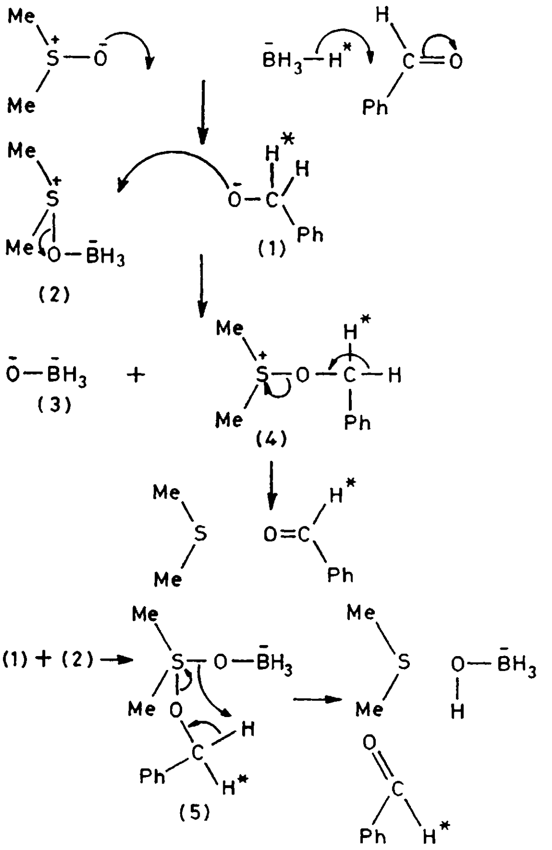
Summary The reduction of benzaldehyde by sodium borohydride in ^{14}C-labelled dimethyl sulphoxide causes the formation of a small quantity of labelled dimethyl sulphide; the relation of this result to current ideas on the mechanism of borohydride reduction is discussed.

SOME time ago Gold and his co-workers reported the incorporation of tritium into recovered benzaldehyde from labelled sodium borohydride in dimethyl sulphoxide solvent.[1–3] In connection with this result, we now report the formation of labelled dimethyl sulphide from dimethyl sulphoxide in the same reaction, and comment on the mechanistic significance of these two results for sodium borohydride reductions conducted in both hydroxylic and non-hydroxylic solvents.

A reduction mixture of benzaldehyde and sodium borohydride was prepared under conditions similar to those used by Gold and his co-workers[1–3] using ^{14}C-labelled dimethyl sulphoxide as solvent. Unlabelled dimethyl sulphide was subsequently added, and the total dimethyl sulphide was recovered by distillation and assayed for radioactivity. Two types of control experiments were necessary in order to obtain meaningful results. The first omitted the borohydride thereby measuring the extent of co-distillation of dimethyl sulphoxide and the possibility of oxygen exchange between dimethyl sulphoxide and dimethyl sulphide. The second omitted the benzaldehyde in order to test for direct reduction of dimethyl sulphoxide by borohydride. Both control experiments showed significant activities in the product, although these were considerably lower than the experiment involving all the reagents (*e.g.* 100—150 d.p.m./ml *vs.* 500 d.p.m./ml). After correction for the controls, the experiment indicated a 0·027% transfer of activity from dimethyl sulphoxide to dimethyl sulphide, a result very similar to the transfer of tritium from borohydride to benzaldehyde reported by Gold[3] (0·034%).[†]

This new exchange result may be accommodated by the mechanisms in the Scheme, which are consistent with previous mechanistic work in borohydride chemistry. Borohydride reduction of benzaldehyde together with nucleophilic participation of the solvent[4] (in this case Me$_2$SO) would give the alkoxide ion (**1**) and an adduct (**2**) of Me$_2$SO and the borane. Attack by the alkoxide on the sulphur atom of (**2**) would give the anion of the monohydroxyborohydride species (**3**) (which, after transfer of all four hydrides, would be orthoboric acid) and the alkoxysulphonium salt (**4**). Species of type (**4**) are known; they are intermediates in the Moffatt oxidation, and are known to collapse to (re)-form the carbonyl compound (benzaldehyde) and dimethyl sulphide.[5] Alternatively (**1**) and (**2**) could add to give (**5**), avoiding the dianion (**3**), and (**5**) could collapse to give the same products.



SCHEME

The key point of this mechanism is the suggestion that borohydride could effect reduction of dimethyl sulphoxide with benzaldehyde acting as the relay.

Because of the similar extent of isotope exchange in both the original[1–3] and the present work, it is tempting to conclude that the same process is responsible for both. This is at present not established. It is, however, noteworthy that the mechanism in the Scheme does accommodate both the tritium exchange and the ^{14}C exchange result. The completely different rationalization for the tritium exchange result previously suggested (non-concerted reaction)[1–3] does not accommodate the ^{14}C exchange result and would require that this arises by a different reaction. Further work is required to resolve this question.

The limitations of both experiments, however, must be clearly recognized. Essentially all previous mechanistic work on borohydride reductions (and the majority of synthetic work) has been conducted using hydroxylic

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[†] % conversion per mole of hydride for experiments conducted for comparable lengths of time. In this particular case run 2 of ref. 3.

solvents. The isotope exchange experiments have been conducted, in part,[1,3] in non-hydroxylic solvent and this change is likely to be a profound one. Thus these results do not rule out mechanisms under current consideration for borohydride reductions in hydroxylic solvents. Indeed, as has already been pointed out,[3] and as is required by the experimental evidence,[4,6,7] some of these mechanisms[6,7] involve molecular participation of the hydroxylic solvent and thus could not possibly occur in non-hydroxylic solvent.

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[1] C. Adams, V. Gold, and D. M. E. Reuben, *J.C.S. Chem. Comm.*, 1977, 182.
[2] C. Adams, V. Gold, and D. M. E. Reuben, *J.C.S. Perkin II*, 1977, 1466.
[3] C. Adams, V. Gold, and D. M. E. Reuben, *J.C.S. Perkin II*, 1977, 1472.
[4] D. C. Wigfield and F. W. Gowland, *J. Org. Chem.*, 1977, **42**, 1108.
[5] A. H. Fenselau and J. G. Moffatt, *J. Amer. Chem. Soc.*, 1966, **88**, 1762.
[6] D. C. Wigfield and F. W. Gowland, *Tetrahedron Letters*, 1976, 3373.
[7] D. C. Wigfield, *Tetrahedron Report* No. 61, *Tetrahedron*, 1979, **35**, 449.