Tritium Exchange between the Aldehyde Group and Sodium Borohydride during the Reduction of Benzaldehyde in Dimethyl Sulphoxide Solution

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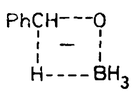
Summary Hydrogen exchange has been observed between tritiated sodium borohydride and the aldehyde group of benzaldehyde, and is interpreted as due to a reverse hydride transfer (as a cage reaction) between borane and benzoxide ion, the primary products of the reduction.

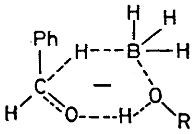
Unreduced benzaldehyde, recovered from reduction experiments with sodium [^{3}H]borohydride in Me_2SO or in Me_2SO–water mixtures as solvent, is found to contain tritium in the aldehyde group. The tritium content increases as the reduction proceeds. The initial rates are consistent with the occurrence of a second-order reaction between benzaldehyde and sodium borohydride, and they show a similar dependence on solvent composition as do rates of reduction.

The observations require reversibility at some stage of the reduction so as to lead back to benzaldehyde. Because of the strong exothermicity of the formation of boron–oxygen bonds it seems highly improbable that reversal could occur after the formation of such bonds. Accordingly we infer that the hydride transfer from hydridoborate species to the aldehyde is reversible. Furthermore, the first such hydride transfer must precede the formation of a boron–oxygen link, and it cannot be concerted with it.

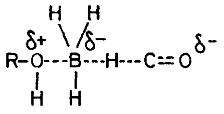
On these grounds reduction mechanisms involving four- or six-membered cyclic transition states (**1**)[1] and (**2**)[2] and the linear transition state (**3**)[3] can be ruled out, since all three imply simultaneous hydride transfer and boron–oxygen bond formation.



(1)



(2)



(3)

On the other hand, neither can one formulate the reaction in terms of a simple reversible first reaction step [reaction (1)],[4] since attempts to establish the presence of borane in these reactions in Me_2SO solutions (in contrast to reactions in diglyme solutions[3,5]) by trapping with amine

$$BH_4^- + PhCHO \rightleftharpoons BH_3 + PhCH_2O^- \qquad (1)$$

proved negative. Accordingly we envisage the products of reaction (1), in the forward direction, to undergo further reaction within the solvent cage in which they were formed before bimolecular reactions with another species, such as an amine, can take place. Two important processes between BH_3 and benzoxide ion that can occur within the cage are reactions (2) and (3). The product of reaction (2)

$$BH_3 + PhCH_2O^- \rightarrow PhCH_2OBH_3^- \qquad (2)$$

$$BH_3 + PhCH_2O^- \rightarrow BH_4^- + PhCHO \qquad (3)$$

is itself a hydride donor and will react further, to yield ultimately the reduction product, $NaB(OCH_2Ph)_4$, which we have isolated from reduction experiments in Me_2SO solution. Reaction (3) re-forms the starting materials and, if tritium-labelled borohydride was used in the reaction, will lead to tritium–labelled benzaldehyde. After allowing for a kinetic isotope effect, we estimate that reaction (2) is between 8 and 20 times faster than reaction (3).

A secondary, more rapid, hydrogen exchange reaction occurs between benzaldehyde and sodium [α-^{3}H]tetrabenzoxyborate.

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