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THE MECHANISM OF BOROHYDRIDE REDUCTIONS. REACTIONS OF GAS PHASE BOROHYDRIDE ION WITH CARBONYL GROUPS BY ION CYCLOTRON RESONANCE SPECTROSCOPY.

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ABSTRACT

The reaction between BH_4^- and CH_2O has been investigated in the gas phase using ion cyclotron resonance spectroscopy. No hydride transfer from BH_4^- to the carbonyl group is observed, however a novel reaction between enolate ions and diborane has been observed.

Reduction of the carbonyl function by borohydride is an important synthetic reaction. In spite of extensive use, a great number of studies and much polemics, the mechanism of this reaction remains somewhat puzzling.[3]

Originally, both single-step and two-step mechanisms were considered as possible reaction pathways. Lately, a single-step, four-centre transition state was ruled out since it could not explain certain experimental results,[4] and is moreover forbidden in terms of orbital symmetry.[5] In the meantime a two-step mechanism enjoyed continuing consideration.[6] Dewar and McKee's MNDO/3 calculations[7] for BH_4^- addition to formaldehyde supported strongly a two-step process; the first step. involving a hydride transfer from BH_4^- to the carbonyl group, followed by formation of B-O bond (equation 1).

$$BH_4^- + H_2CO \xrightarrow{\text{step 1}} BH_3 + CH_3O^- \xrightarrow{\text{step 2}} CH_3O\text{-}\bar{B}H_3 \qquad (1)$$

More recently, <u>ab initio</u> calculations carried out for concerted and stepwise pathways for the reduction of H_2CO by BH_4^- showed that, while

Dewar and McKee's overall mechanism is exothermic, the first step, the complete hydride transfer, is endothermic by 36 kcal mol^{-1}. These latter calculations suggest that the more favourable path is a single-step mechanism with a four center transition state best described as a BH_3 group bridging the newly formed C-H bond and the carbonyl oxygen atom. This pathway is exothermic with a 30 kcal mol^{-1} energy barrier. The calculations are however in contrast with the experimental observation that the reductions of aldehydes by BH_4^- in solution are rapid and exothermic with no apparent energy barrier. Evidently, such behaviour might be due to solvent effects. To investigate this possibility ab initio calculations were performed for the reduction involving solvation of each reactant and product by a single molecule of water.[8] While the calculated activation barrier for this process was lowered it remained a substantial 21 kcal mol^{-1}. Significantly, only when a counter ion was included (equation 2) did the hydride transfer from BH_4^- to H_2CO become exothermic.

$$Na^+ \cdot BH_4^- + H_2CO \rightarrow Na^+ \cdot CH_3O^- + BH_3 \qquad (2)$$

In order to better understand the reaction of BH_4^- with H_2CO and with carbonyl functions in general and to determine whether or not an intrinsic activation barrier exists in the borohydride reductions of carbonyl compounds, the present ion cyclotron resonance (ICR) study was undertaken.

Borohydride ion, BH_4^-, was generated in the ICR apparatus by the reaction of F^-, produced via dissociative electron attachment to NF_3, with diborane, B_2H_6. This reaction yielded in addition to BH_4^- small quantities of BH_3F^- and $B_2H_5^-$, (equation 3). Subsequent addition of formaldehyde to the system revealed no reaction of any boron containing anions

$$F^- + B_2H_6 \begin{cases} \rightarrow BH_4^- + BH_3F & (3a) \\ \rightarrow BH_3F^- + BH_3 & (3b) \\ \rightarrow B_2H_5^- + HF & (3c) \end{cases}$$

with H_2CO. In particular no hydride transfer from BH_4^- to H_2CO was observed, (equation 4). Reaction of CD_3O^- with B_2H_6 led rapidly to

$$BH_4^- + H_2CO \not\rightarrow BH_3 + H_3C\text{-}O^- \qquad (4)$$

production of BH_4^- but no BH_3D^- via reaction (5).[9] A much slower reaction, eqn (6),

$$CD_3O^- + B_2H_6 \rightarrow BH_4^- + CD_3OBH_2 \qquad (5)$$

to yield $B_2H_6D^-$ was also observed indicating

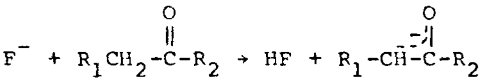
$$CD_3O^- + B_2H_6 \rightarrow B_2H_6D^- + CD_2O \qquad (6)$$

that B_2H_6, and probably BH_3', has a greater hydride affinity than CH_2O giving further weight to the suggestion that eqn (4) is endothermic. Attempts to "activate" the carbonyl group by substituting electronegative groups for hydrogen at the carbonyl centre were similarly unsuccessful. For example, in the presence of F_2CO, BH_4^- exhibited no gas phase reactivity, (equation 7). The gas phase data thus support the results of the *ab initio* calculations[8] showing the reaction of naked BH_4^- with

$$BH_4^- + F_2CO \not\longrightarrow BH_3 + F_2CHO^- \qquad (7)$$

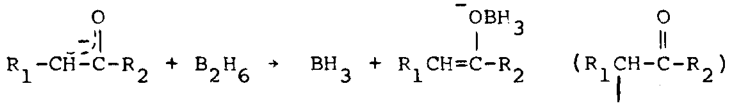
formaldehyde to be highly endothermic. They suggest that hydride transfer from BH_4^- to a carbonyl function is intrinsically either endothermic or, if exothermic, then involves a significant activation energy. Thus the problem of one versus two-step mechanism remains unresolved. It appears evident that in solution the borohydride reduction of carbonyl compounds must proceed with solvent and/or counter ion participation.

Despite the failure to distinguish between two possible reaction mechanisms, an extremely interesting gas phase ion-molecule reaction was observed in mixtures of carbonyl compounds and diborane, B_2H_6. In the presence of carbonyl compounds with α-hydrogen atoms, F^- undergoes exothermic proton abstraction in the gas phase, (equation 8).[10] The resulting enolate ion subsequently reacts with diborane to produce a new boron enolate ion,



$$F^- + R_1CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R_2 \rightarrow HF + R_1\text{-}\bar{C}H\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R_2 \qquad (8)$$

(equation 9). These novel boron enolate anions have known analogues in solution synthetic chemistry where



$$R_1\text{-}\overset{-}{C}H\text{-}\overset{\overset{O}{\|}}{C}\text{-}R_2 + B_2H_6 \rightarrow BH_3 + R_1CH{=}\overset{\overset{^{-}OBH_3}{|}}{C}\text{-}R_2 \quad (R_1\underset{\underset{-BH_3}{|}}{C}H\text{-}\overset{\overset{O}{\|}}{C}\text{-}R_2) \qquad (9)$$

trialkylboron enolates are used as stereoselective reagents in reactions such as reductions or aldol condensations,[11] although in the gas phase we are unable to determine, as yet, whether BH_3 addition occurs at oxygen or carbon.

Further contributions from this laboratory will provide a more extensive documentation and analysis of this reaction and related reactions of a wide variety of anions with diborane.

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