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MNDO Study of Reaction Paths: Diboration of Acetylene

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The reaction of B_2H_4 with acetylene has been studied by the MNDO method. It is shown that the reaction is exothermic and proceeds in two steps. The first step is the formation of a three-center π-complex and this is the rate-determining step of the reaction. The second step is the rearrangement of the π-complex to the product and this step requires a very small amount of activation energy. The activation barrier for the diboration reaction is 12.8 kcal/mol.

The proposed mechanism is significantly different from those proposed earlier and explains all experimental data relating to this reaction.

Key words: Diboration of acetylene – Three-center π-complex – Charg-transfer effects.

1. Introduction

One of the most interesting and characteristic additions of the diboron tetrahalides is their ready addition across carbon–carbon double and triple bonds. This process, which has been called "diboration" [1] by analogy to the well-known hydroboration reaction, provides a convenient route to vicinal bis(dihaloboryl) organic derivatives. The resulting compounds may be converted to other bis (boryl) derivatives by a variety of reactions, by oxidative hydrolysis to vic-diols, or, in certain cases, to hydrocarbons by protonolysis.

No detailed study of the mechanism of this very important reaction has been carried out yet, although it is commonly presumed [2, 3] that the reaction occurs

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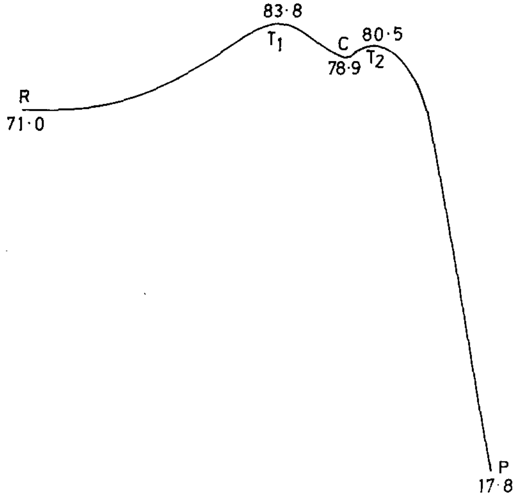


Fig. 1. The energy profile (kcal/mole) for the reaction of acetylene with diborane. The B_1C_2 bond (see Fig. 2) distance was employed as the reaction coordinate

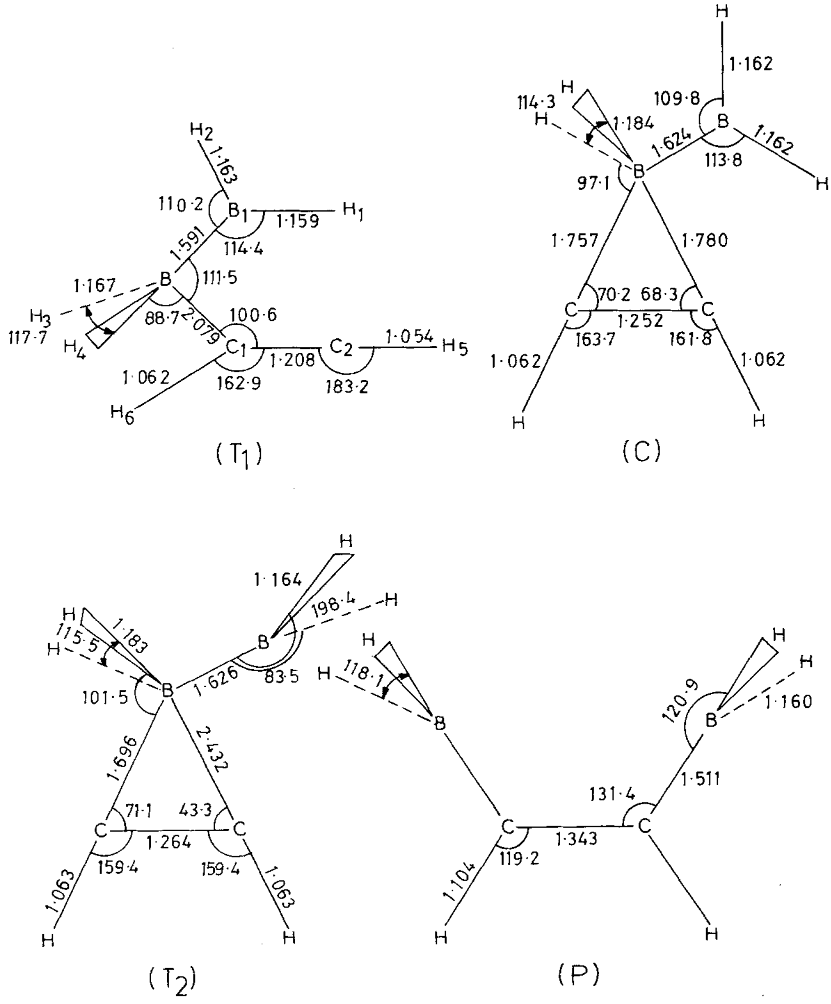
via a four-center mechanism. In the present work, we have performed MNDO calculations [4] on the reaction of B_2H_4 with acetylene. Here, B_2H_4 has been used as a prototype for diboron tetrahalides.

2. Method of Calculation

The MNDO method with the usual parameters [4, 5] was used for all the calculations reported here. The B_1C_2 distance was employed as the reaction coordinate and the heat of formation of the supermolecule (acetylene + B_2H_4) was plotted against this distance (see Fig. 1). According to Rothman and Lohr [6], the maxima on such reaction surfaces are transition states, provided the reaction pathway is continuous. These transition state geometries, as well as the geometries of equilibrium points, are shown in Fig. 2.

3. Results and Discussion

The reaction profile is shown in Fig. 1. There are three stationary points, besides the reactants and the product, on the reaction surface. These three points are: one minimum (the complex, C) and two maxima, one T1, leading to the complex, and the other, T2, leading to the product, P. The optimized structures of these three points, shown in Fig. 2, reveal that C and T2 are both three-center type structures. The first stage of the reaction involves the interaction of one of the BH_2 groups (the one in which the hydrogens are not in the plane containing the rest of the atoms) with acetylene, resulting in the formation of a three-center complex. Because of steric reasons, this BH_2 group can approach the π-system of acetylene more closely than the other one. This step is the rate-determining step of the reaction and requires an activation energy of 12.8 kcal/mol. The complex is less stable than the reacting species by 7.9 kcal/mol. The second step of the reaction is the attachment of the other BH_2 group to a carbon atom. This



(T1) (C)

(T2) (P)

Fig. 2. The optimized geometries (in angstroms and degrees) for the transition state (T1) for the formation of complex, the complex (C), the transition state (T2) for the formation of product, and the product (P)

step requires an activation energy of 1.6 kcal/mol. As the second BH_2 group approaches the π-system, it rotates about the B—B bond until it also comes out of the plane of the boron atoms and the acetylene moiety.

The mechanism proposed here is in agreement with experimental observations. It leads to cis addition, as has been observed experimentally [7]. Acetylene reacts readily with B_2Cl_4, at room temperature, to form the 1 : 1 diboration product [8]. The formation of a complex in the reaction of acetylene with B_2Cl_4 has been observed experimentally by Urry [1]. He has mentioned the formation, at −80°C, of a solid complex from which the reagents can be recovered, and which slowly reacts to form the 1 : 1 diboration product.

This mechanism differs appreciably from other mechanisms proposed [7] for this reaction. Many workers [2, 3] have presumed that the addition reaction proceeds via donation from the olefin into the vacant *p* orbitals of the diboron compound, followed by the rupture of the boron–boron bond and simultaneous formation of two boron–carbon σ bonds. Although this mechanism is in agreement with the stereochemistry of the reaction, it entails distortion of the diboron molecule from the skewed (D_{2d}) equilibrium configuration to the planar (D_{2h}) configuration, prior to the formation of the complex. The barrier for this rotation is expected to be quite high. In the three-center mechanism proposed by us, this rotation occurs only in the second step, by which time the B—B bond is considerably weakened. An alternative reaction pathway, involving heterolytic cleavage of the B—B bond might be expected to lead to trans addition product. The formally similar electrophilic addition of halogens to simple olefins is, of course, well known to lead to trans addition. This type of mechanism seems unlikely on two counts. It does not explain the stereochemistry of the reaction. Secondly, the effect of substituents on the rate of diboration of olefins does not parallel that observed in the bromination reactions [7].

The structure of the product, shown in Fig. 2, indicates that both the BH_2 groups are perpendicular to the plane of the carbon and boron atoms. However, calculations indicate that the most stable configurations of the BH_2 groups is one in which one group is planar and the other nonplanar. Therefore, it is possible that the initially formed product rearranges to this, more stable, one (the difference in stabilities is 1.1 kcal/mol). The exothermicity of the reaction is −53.2 kcal/mol.

4. Charge-transfer Effects

In Table 1 are presented the charges on various atoms at the different stages of the reaction. The first transition state, T1, is at a fairly early stage in the reaction,

Table 1. Charges on various atoms at different points on the reaction surface

	Charge (Q)				
Atom[a]	R	T1	C	T2	P
B_1	0.08	0.10	0.22	0.22	0.19
B_2	0.08	−0.04	−0.44	−0.45	0.19
C_1	−0.16	−0.14	0.04	0.01	−0.13
C_2	−0.16	−0.05	0.01	0.03	−0.13
H_1	−0.04	−0.08	−0.10	−0.09	−0.06
H_2	−0.04	−0.06	−0.07	−0.08	−0.06
H_3	−0.04	−0.04	0.00	0.02	−0.06
H_4	−0.04	−0.04	0.00	0.02	−0.06
H_5	0.16	0.17	0.17	0.16	0.06
H_6	0.16	0.18	0.17	0.16	0.06

[a] See Fig. 2 for numbering.

and the main effect on going from the reactants to T1 is the transfer of 0.11 units of charge from C_2 to B_2 (see Fig. 2). The net charge transferred from the acetylene moiety to the B_2H_4 moiety is 0.16 units. At the complex, the charge transferred becomes equal to 0.39 units. The main effect is on B_2, which gains in negative charge by 0.52 units, 0.14 units of which come from B_1, 0.20 from C_1 and 0.17 from C_2. At T_2, the net charge transferred is 0.36. Thus, T_2 resembles the complex very closely.

Hence, the adduct is a π-complex, in which there is donation of charge density from the π-system of acetylene to one of the boron atoms (not both, as commonly believed).

The transition state for the second step is at a very early stage of the step, and resembles the π-complex.

Three-center electron-deficient bonds, such as those in the complex, are not uncommon in boron chemistry and may be regarded as being formed by the interaction of a BH_2 moiety with the acetylenic π-bond, such that the 2p orbitals of the acetylene carbon atoms overlap with the vacant $2p$ orbitals of the boron atom. There is enough experimental evidence to indicate the involvement of the boron $2p$ orbitals. For example, (B_2Cl_4-base) complexes are unreactive towards diboration [9], as are compounds such as the aminodiborons in which the coordinative saturation of the boron atoms can be removed or reduced by $p\pi - p\pi$ bonding.

5. Conclusions

In conclusion, we have shown that the commonly accepted four-center mechanism for diboration is incorrect. The reaction proceeds via a three-center mechanism and occurs in two stages, of which the first is the rate-determining step. The conversion of the three-center π-complex to the product occurs very easily and requires a small amount of activation energy.

This mechanism is significantly different from any mechanism proposed before, and explains all experimental information regarding this reaction. It may also be seen that this mechanism is similar to that found by Dewar and McKee for the hydroboration of acetylene [10].

All calculations were carried out on the IBM 360/44 computer at the Delhi University Computer Centre.

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