

MNDO study of reaction paths : Hydroboration of carbonyl systems

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Abstract. The hydroboration reactions of acetaldehyde and acetone have been investigated by the MNDO method. The reactions have been shown to be two-step reactions involving an intermediate adduct. This adduct subsequently undergoes hydrogen rearrangement. The hydroboration reactions of acetaldehyde and acetone have been compared with the corresponding reaction of formaldehyde. The charge transfer effects accompanying these reactions have also been discussed.

Keywords. Hydroboration of acetaldehyde and acetone; effect of methyl substitution; charge transfer effects.

1. Introduction

In the year 1939, Brown *et al* demonstrated that diborane reacts rapidly with simple aldehydes and ketones, such as acetaldehyde and acetone, to produce the corresponding dialkoxyboranes (Brown *et al* 1939). Since these substances are readily hydrolysed to form acid and the corresponding alcohol, it is evident that the procedure offers a promising route for the reduction of carbonyl groups. For this reason, we have undertaken a theoretical study on the hydroboration of carbonyl systems.

The results of our study on the hydroboration of formaldehyde (Ray and Chadha 1981) had shown that the reaction is a two-step reaction involving the initial formation of an adduct, followed by its rearrangement to the product *via* a four-centre-like transition state. This latter step was shown to be the rate-determining step. In the present work, we have carried out calculations on the reaction of borane with acetaldehyde and acetone.

2. Method of calculation

The Modified Neglect of Diatomic Overlap (MNDO) method with the usual parameters (Dewar and Thiel 1977; Dewar and McKee 1977) was employed for

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all the calculations reported here. For the methyl group, C_{3v} symmetry was maintained throughout the calculations. All other geometrical parameters were completely optimized. The transition states were located by the energy minimization method (Rothman and Lohr 1980). The incipient C-H bond length was employed as the reaction coordinate and the heat of formation of the systems was plotted as a function of this reaction coordinate. Rothman and Lohr (1980) have shown that the maxima obtained on such reaction surfaces are transition states, provided that the reaction pathway is continuous. The force constant matrix at such points also has only one negative eigenvalue.

3. Results and discussion

The reaction profile for the hydroboration reaction of acetaldehyde with borane (figure 1) indicates two transition states and one intermediate along the reaction pathway. Hence, like the corresponding reaction of formaldehyde, this is a two-step reaction, involving the initial formation of an adduct as a stable intermediate. The activation energy required for its formation is 26.5 kcal/mol, a value much higher than that found (Ray and Chadha 1981) for formaldehyde (9.7 kcal/mol). Thus, the substitution of a hydrogen atom in formaldehyde by a methyl group results in a considerable increase in the activation energy required for the first step. The adduct is more stable than the reactants by 9.5 kcal/mol (c.f. 9.2 kcal/mol for formaldehyde). Methyl substitution, therefore, has only a small effect on the relative stabilities of reactants and adduct. The activation barrier for the second step increases to 28.2 kcal/mol. The reaction enthalpy is -43.1 kcal/mol.

Figure 2 gives the optimized geometries of the four stationary points on the reaction surface. As in the case of formaldehyde, the carbon-oxygen bond distance increases as the reaction proceeds. The B-O bond distance decreases to 1.50 Å in the adduct, after which it increases to a value of 1.53 Å in T_2 , and

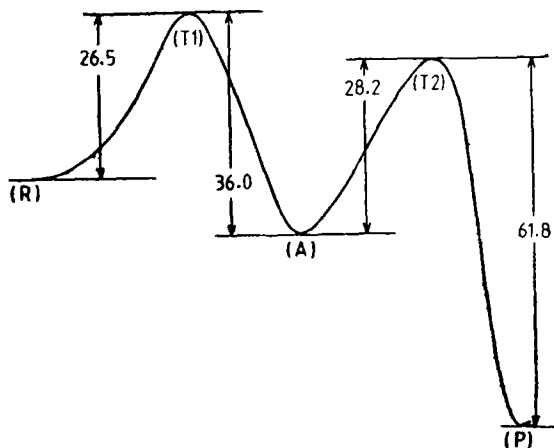


Figure 1. The energy profile (kcal/mol) for the reaction of acetaldehyde with borane.

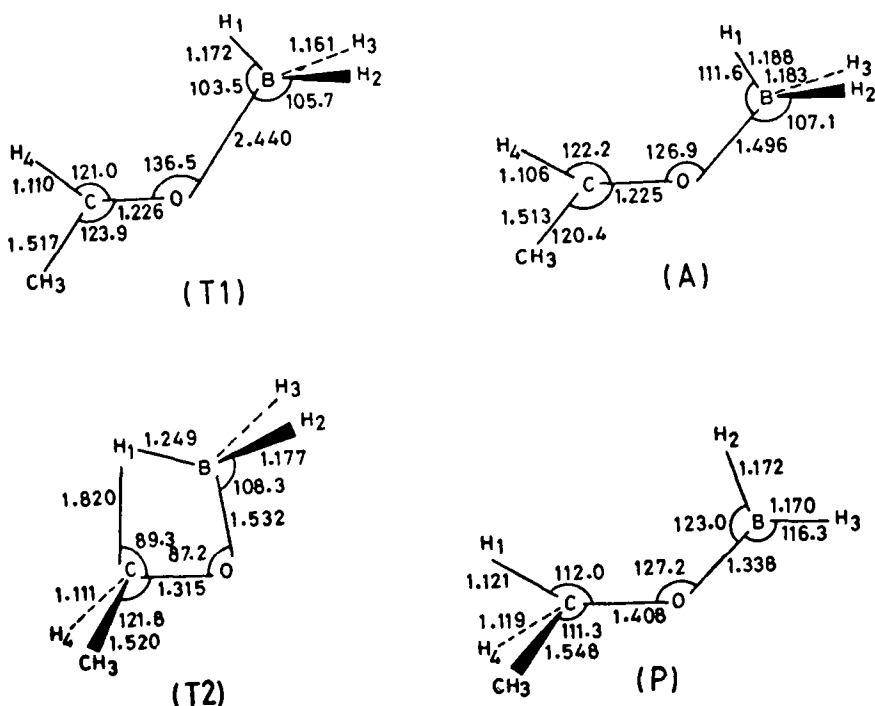


Figure 2. The optimized geometries (in angstroms and degrees) for the transition state (*T1*) for formation of the adduct, the adduct (*A*), the transition state (*T2*) for the formation of product (*P*) for the hydroboration of acetaldehyde.

then decreases again to a value of 1.34 \AA in the product. The COB bond angle decreases from its value of 136.5° in *T1* to 87.2° in *T2*, after which it increases to 127.2° in the product. In this case, too, *T2* has a four-centre-like structure.

The hydroboration reaction of acetone, which is the simplest ketone, has also been studied. The profile of this reaction is similar to that of the corresponding reaction of acetaldehyde (figure 3). The first step, the formation of adduct, requires an activation energy of 26.4 kcal/mol . Therefore, the activation barrier for the first step is almost the same for the hydroboration of acetaldehyde and acetone. The second step proceeds with an activation energy of 31.3 kcal/mol . The reaction enthalpy is -36.2 kcal/mol .

Figure 4 gives the optimized geometry of each stationary point on the reaction surface. As expected, the carbon-oxygen bond distance increases as the reaction proceeds. The B-O bond distance is 1.49 \AA in the adduct, after which it increases to a value of 1.52 \AA in *T2*, and then decreases to 1.34 \AA in the product. The COB bond angle also decreases from its value of 144.7° in *T1* to 89.2° in *T2*, after which it increases to 126.9° in the product. *T2* again has a four-centre-like structure. Comparison of figure 2 with figure 4 indicates that the geometries at the stationary points are essentially similar for both the reactions studied here. For the sake of comparison, the energetics of both the reactions are listed in table 3. Although the energy of activation for the rate-determining step increases with methyl substitution, the effect is not very pronounced.

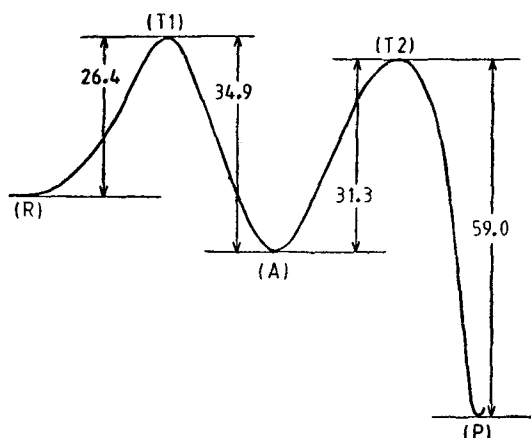


Figure 3. The energy profile (kcal/mol) for the reaction of acetone with borane.

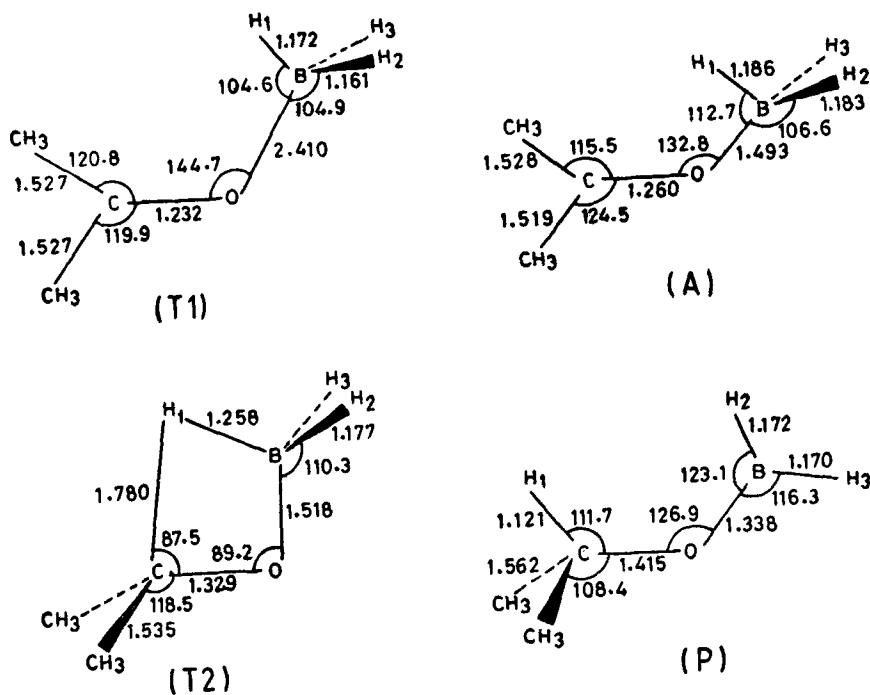


Figure 4. The optimized geometries (in angstroms and degrees) for the stationary points on the reaction surface for hydroboration of acetone.

4. Charge transfer effects

The charges on various atoms in the stationary points on the potential surface for hydroboration of acetaldehyde are presented in table 1. In *T1*, the amount of electronic charge transferred from the acetaldehyde moiety to the borane moiety is only 0.03 units, signifying that *T1* is formed in a fairly early stage of the reaction.

Table 1. Charges on various atoms in the stationary points on the reaction surface^a for hydroboration of acetaldehyde.

Atom ^b	Charge				
	R	T1	A	T2	P
C	0.24	0.27	0.29	0.41	0.17
O	-0.28	-0.31	-0.03	-0.24	-0.25
B	0.24	0.23	-0.21	-0.15	0.11
H ₁	-0.08	-0.13	-0.12	-0.11	0.00
H ₂	-0.08	-0.09	-0.06	-0.03	-0.05
H ₃	-0.08	-0.04	-0.07	-0.03	-0.02
H ₄	0.01	0.03	0.09	0.06	0.02
CH ₃	0.03	0.04	0.11	0.09	0.02

^a see figure 1^b see figure 2.Table 2. Charges on various atoms in the stationary points on the reaction surface^a for hydroboration of acetone.

Atom ^b	Charge				
	R	T1	A	T2	P
C	0.19	0.23	0.25	0.39	0.13
O	-0.29	-0.31	-0.04	-0.26	-0.24
B	0.24	0.23	-0.20	-0.13	0.10
H ₁	-0.08	-0.13	-0.12	-0.14	0.02
H ₂	-0.08	-0.09	-0.07	-0.03	-0.05
H ₃	-0.08	-0.05	-0.07	-0.03	-0.02
(CH ₃) ₁	0.05	0.06	0.11	0.10	0.03
(CH ₃) ₂	0.05	0.06	0.14	0.10	0.03

^a see figure 3^b see figure 4

Table 3. Heats of formation at stationary points on the reaction surface^a for hydroboration of carbonyl systems.

Point	Heat of formation (kcal/mol)	
	Acetaldehyde	Acetone
<i>R</i>	-30.6	-37.1
<i>T1</i>	-4.1	-10.7
<i>A</i>	-40.1	-45.6
<i>T2</i>	-11.9	-14.3
<i>P</i>	-73.7	-73.3
<i>EA</i> ^b (kcal/mol)	28.2	31.3

^a see figures 1 and 3.

^b Energy of activation for the rate-determining step.

The progress of the reaction from *T1* to *A* is accompanied with an increase in charge density on the boron atom by 0.44 units. The total amount of charge transferred from acetaldehyde to borane, in the adduct, is 0.46 units. In *T2*, the amount of charge transferred reduces to 0.32 units, due to back donation of charge to the oxygen atom.

The charges on various atoms in the stationary points on the potential surface for hydroboration of acetone are listed in table 2. In this case, the amounts of charge transferred from acetone to borane in *T1*, *A* and *T2* are, respectively, 0.04, 0.46 and 0.33 units.

In all the cases, therefore, the adduct is a charge transfer complex and the amount of charge transfer from the carbonyl system to borane is nearly constant.

5. Conclusions

The present study has indicated that the reaction path for the hydroboration of aldehydes and ketones includes an intermediate charge transfer adduct and two transition states. The pronounced effect of substitution of one hydrogen atom of formaldehyde by a methyl group on the activation barrier to the first step is probably due to steric factors. Unlike the case of nitriles (Chadha and Ray 1982) the transition state for the first step is more susceptible to steric hindrance.

The results of the present work are in agreement with the mechanism proposed by Brown and Subba Rao (1960). As expected, methyl substitution increases the stability of the adduct (table 3). The electron donating property of the methyl group is responsible for this effect. Like the hydroboration reaction of formaldehyde, for both reactions studied here, *T1* is formed in a fairly early stage of the reaction and resembles the separated reactants very closely in its electronic structure.

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