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MNDO Study of Reaction Paths: Hydroboration of Methyl Cyanide

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The hydroboration reaction of methyl cyanide has been investigated by the MNDO method. It has been shown that the reaction requires an activation energy of 25.3 kcal/mol and involves a four-center-like transition state in the rate-determining step. This reaction has been compared with the corresponding reaction of hydrogen cyanide, and the effect of methyl substitution on the reaction has been discussed. The charge-transfer effects accompanying the reaction have also been studied.

Key words: Hydroboration of methyl cyanide – Effect of methyl substitution – Charge-transfer effects.

1. Introduction

In the last few years, considerable effort [1–4] has been made to deduce the mechanism of hydroboration reactions. Nagase et al. [4] found that the reaction of ethylene with borane involves a two-step mechanism and that the transition state for the rate-determining second step has a four-center-like structure. Subsequently, Chadha and Ray [5] carried out a study on the hydroboration of hydrogen cyanide. Again, a four-center-like transition state was found to be involved in the rate-determining step of the reaction.

In the present work, we have studied the hydroboration reaction of methyl cyanide using the MNDO method. The object of this study was to determine the effect of methyl substitution on the reaction rate of hydroboration reactions.

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2. Method Calculation

The MNDO method with the usual parameters [6, 7] was employed for 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 for the reaction were located by the energy minimization method [8]. The forming C—H$_1$ bond length (see Fig. 1) was employed as the reaction coordinate and the heat of formation of the system was plotted as a function of this reaction coordinate. Rothman and Lohr [8] have pointed out that the maxima obtained on such reaction surfaces are transition states, provided that the reaction pathway is continuous in that region. According to these authors, the force constant matrix at such points has only one negative eigenvalue.

3. Results and Discussion

The optimized geometries of the local minima and transition states for the hydroboration of hydrogen cyanide [5] were used as starting points for geometry search. The optimized geometries of the transition state (*T*1) for the formation of the adduct, the adduct (*A*), the transition state (*T*2) for the formation of product and the product (*P*) are shown in Fig. 1. It can be seen that these geometries are essentially similar to those found for the hydroboration of hydrogen cyanide.

The heats of formation of the reactants, *T*1, *A*, *T*2 and *P* are, respectively, 30.5, 34.5, 11.0, 55.8 and −4.7 kcal/mol. Thus the activation energy barrier for the reaction is 25.3 kcal/mol, a value 4.0 kcal/mol higher than that for hydrogen cyanide. In the first step, methyl substitution increases the activation energy by only 0.2 kcal/mol. (For HCN the activation barrier for the first step is

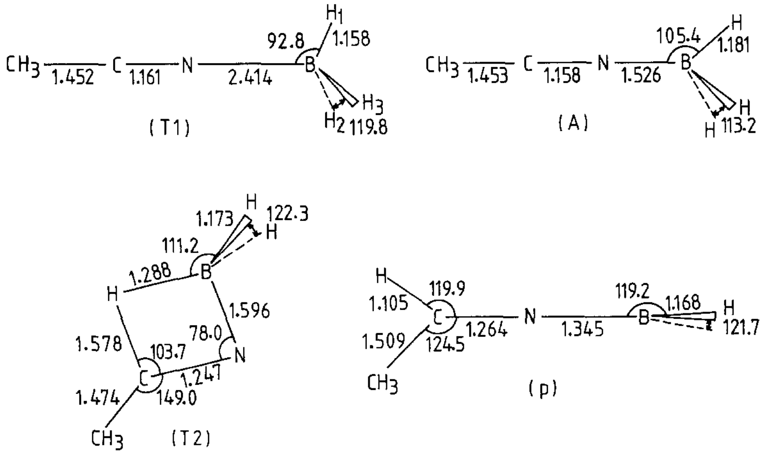

Fig. 1. The optimized geometries (in angstroms and degrees) for the transition state (*T*1) for formation of the adduct, the adduct (*A*), the transition state (*T*2) for the formation of product, and product (*P*)

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

	Charge (Q)				
Atom[a]	R	$T1$	A	$T2$	P
C	−0.11	−0.08	0.02	0.10	0.18
N	−0.08	−0.10	0.11	−0.07	−0.31
B	0.24	0.22	−0.17	−0.16	0.06
H_1	−0.08	−0.08	−0.07	0.00	−0.01
H_2	−0.08	−0.08	−0.07	0.00	−0.01
H_3	−0.08	−0.08	−0.07	−0.06	0.04
CH_3	0.19	0.20	0.25	0.19	0.05

[a] See Fig. 1 for numbering of hydrogens.

3.8 kcal/mol, while for CH_3CN the corresponding number is 4.0). The heat of reaction for the first step is −19.5 kcal/mol (cf. −19.8 kcal/mol in the case of hydrogen cyanide). The net heat of reaction is −35.2 kcal/mol (cf. −41.4 kcal/mol for hydrogen cyanide).

Since the second step is the rate-determining one, and this step involves a four-center-like transition state, steric factors are likely to predominate in the reaction. Hence, it is possible that the increase in activation energy on methyl substitution may be due to steric, rather than electronic, factors.

Calculated charge density values are listed in Table 1. The amounts of electronic charge transferred from the methyl cyanide moiety to the borane moiety in $T1$, A and $T2$, are, respectively, 0.02, 0.38 and 0.22. These values are very similar to those obtained for the hydroboration of hydrogen cyanide [5]. As in the case of hydrogen cyanide, $T1$ resembles the reactant molecules very closely.

4. Conclusions

In conclusion, our calculations have indicated that the hydroboration reaction of methyl cyanide is very similar to that of hydrogen cyanide. The activation energy for the second (rate-determining) step increases on methyl substitution, probably due to steric hindrance of the methyl group. Thus, methyl substitution is expected to increase the activation energy required for the hydroboration of nitriles.

However, methyl substitution does not lead to any perceptible change in the charge-transfer effects accompanying the reaction.

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