

CNDO CALCULATIONS OF REARRANGEMENTS IN THE $C_3H_7^+$ SERIES

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The formation of protonated cyclopropane (c-Pr) during reactions involving the n-propyl cation (n-Pr) has been well established [1]. MO calculations [2,3] predict the edge protonated c-Pr to be the most stable species. In addition, we reported that n-Pr should collapse to c-Pr without activation energy [2]. The question of possible rearrangements of the isopropyl cation (i-Pr) was left open at that time. Olah recently reported experimental evidence of the equilibration of i-Pr and c-Pr in "magic acid".

In continuation of our investigations in the $C_3H_7^+$ series we have used semiempirical MO calculations to study the rearrangement of i-Pr to c-Pr. The study was performed using our modified CNDO procedure [5], which yields good values for heats of atomization and equilibrium geometries for hydrocarbons and carbonium ions [2,5,6]. The method is especially well suited for calculating reaction paths, because the total energy of a molecular system can be minimized with respect to all bond lengths and angles (with the exclusion of the reaction coordinate).

The main results of our computations may be summarized as follows:

- 1) The ion with the classical isopropyl structure (I) is the only species in the $C_3H_7^+$ series besides c-Pr (V) which belongs to an energy minimum. i-Pr is found to be 14 kcal/mole less stable than V. This value appears reasonable when compared with gas-phase measurements by electron impact [7], but in solution the order of stability seems to be reversed.

2) *n*-Pr does not correspond to an energy minimum. The most stable *n*-propyl configuration (II), obtained by restricting the rotation at C1, is 25 kcal/mole less stable than *i*-Pr, which is in excellent agreement with the results of gas-phase experiments [9]. The rotational barrier at C1 in *n*-Pr is calculated to be no higher than 0.9 kcal/mole (no allowance was made for changing bond lengths and angles during the rotation). In the conformation IIa, in which a C2-H bond is eclipsed to the empty p orbital at C1, *n*-Pr can be transformed to *i*-Pr without activation energy. Similarly, the *n*-Pr conformer IIb, with the C2-C3 bond eclipsed to the empty p orbital, collapses to *c*-Pr without activation energy, as has been shown previously [2].

These results were to be expected on the basis of a study of the MO's involved in the rearrangements. The three-center bonds in the intermediates III and IV can be obtained by a linear combination of the empty p orbital at C1 of II and the eclipsed orbital at C2 which forms the bond to the migrating group (fig. 1).

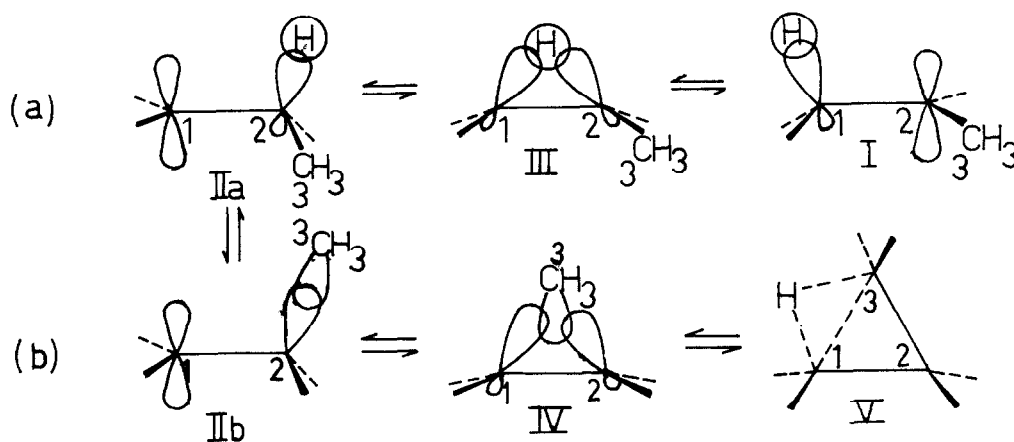


Figure 1: The Rearrangement of the *n*-propyl cation (II) to
 a) the isopropyl cation (I); b) protonated cyclopropane (IV and V)

3) According to our calculations, the protonated propene (III) does not correspond to an energy minimum. With the H atom above the middle of the C1-C2 bond (and minimization

of all other geometric parameters), III is 6 kcal/mole less stable than I. This result is in contrast to NDDO calculations [3], which may be due to the lack of minimization in that case. An energy partitioning analysis [8] reveals that the two bonds between the migrating H atom and C1 and C2 are of unequal strength. The difference is due to the inductive effect of the methyl group.

4) The relative energies and the main features of the equilibrium geometries are listed in table 1 for the $C_3H_7^+$ species which are of interest in this study. The heat of atomization of i-Pr (the enthalpy of the reaction $3C+6H+H^+ \rightarrow i-C_3H_7^+$) is calculated to be 1106 kcal/mole (experimental value: 1050 kcal/mole [9]).

Table 1: Relative Energies and Equilibrium Geometries of various $C_3H_7^+$ species *)

		E_{rel}	Equilibrium geometry		
			C1-C2	C2-C3	\angle 123
I	i-Pr	0	1.49	1.49	130
II	n-Pr	25	1.48	1.53	120
III	prot. propene	6	1.42	1.53	128
IV	Me-bridg. c-Pr	-3	1.44	1.63	63
V	Edge prot. c-Pr	-14	1.52	1.52	67

*) E_{rel} in kcal/mol, $E_{rel}(I) = 0$; bondlengths in Å, angles in degrees

5) Given the low activation energy for the rotation at C1 in n-Pr, it is obvious that fig. 1 shows a possible reaction path for the interconversion i-Pr (I) to the cyclic compound V with an activation energy of 25 kcal/mole and with n-Pr (II) as the transition state.

Thorough computational studies have shown that the reaction path shown in fig. 1 is the path of minimum energy. All processes which include a concerted migration of the methyl group and the H atom are energetically less favorable. The empty p orbital at C1 in II cannot form two effective three center bonds simultaneously with the two occupied hybrid orbitals at the neighboring C2 because of orthogonality requirements.

For the sake of simplicity, it was assumed that the rearrangement of n-Pr to c-Pr proceeds through the methyl-bridged ethylene (IV). This assumption cannot affect the results of the calculations because, for larger C-C-C angles, structures similar to IV

are more stable than those similar to V.

6) In conclusion, the available experimental results should be discussed in the light of our MO study. In $\text{SO}_2\text{ClF-SbF}_5$, a highly ionizing solvent of extremely low nucleophilicity, intramolecular hydrogen exchange between the different positions in i-Pr has been observed [10]. It was demonstrated by Saunders that the measured activation energy could correspond to the reaction $\text{i-Pr} \rightarrow \text{n-Pr}$. Moreover, Olah [4] has shown that ^{13}C scrambling in i-Pr occurs at the same rate as H scrambling, leading to the assumption of an equilibration of i-Pr with c-Pr. These results are in agreement with our calculations, which predict an equilibration of i-Pr with c-Pr via n-Pr. In more nucleophilic solvents the situation is complicated by the larger solvation effects. In fact, neither the rearrangement of i-Pr to c-Pr [1, 11] nor the reverse reaction [12] has been observed in such solvents. This might be due to the short lifetimes of the free cations in such solutions, or it may be that the solvation of the ions results in additional activation energy for the rearrangements of n-Pr.

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