Electronic Structure of Friedel–Crafts Catalysts. Boron Trifluoride and Alkyl Fluoride

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MINDO/3 calculations have been carried out for the species BF_3,FR (R = H, CH_3, C_2H_5, n-C_3H_7, and iso-C_3H_7) with geometrical optimization. Two minima have been found in an exploration of the STO-3G potential hypersurface of BF_3,FH. The role of catalyst is discussed in terms of variation of charge, stabilization of LUMO, and cation-donating capability. Characteristic bicyclic structures are used to interpret isomerization phenomena.

THE species BF_3,FH has been utilized for a theoretical investigation of the catalysed Friedel–Crafts aromatic substitution.[1,2] These articles constitute some of the few papers in which a theoretical interpretation of homogeneous catalysis is attempted, thanks to the correct selection of the catalyst, avoiding the problem which the presence of *d*-orbitals in most Lewis acids habitually causes. We can anticipate increases in the donor capacity of protons, and in their electrophilicity due to the greater charge on hydrogen, as it passes from the HF species to the adduct with BF_3. We expected that the HF could be used as a model for a Friedel–Crafts reactant, where the proton acts as the substituent group.

Both the BF_3,FR adducts and the complexes which form with aromatic compounds have been isolated by Olah and his colleagues, and have been used in investigations on the pathway of electrophilic aromatic substitution.[3,4] The electronic structure of the BF_3,FR adducts gives cause for speculation on its more or less polar nature.[3,4]

One of the most difficult aspects of the interpretation of electrophilic substitution catalysed by Lewis acids is the appearance of different isomers among the final products. Primary alkyl chlorides produce primary and secondary alkylbenzenes and also tertiary alkylbenzenes if a tertiary hydrogen atom is available in the alkyl group. It has been verified that two possible products are obtained in the case of ethyl, when one of the carbon atoms is labelled;[5,6] a non-aromatic symmetrical intermediate is proposed, similar to Olah's σ-complexes.[5] A prior isomerization in the complex formed between the ethyl halides and Lewis acid has also been observed.[6] Attempts have been made to improve the rules for the isomerization which attends alkylation, but there are always some exceptional cases.[7]

It is essential to consider the nature of the alkyl group, both to study the polar nature of the intermediates, which changes as the alkyl group varies, and to try to interpret the aforesaid isomerization phenomena. We have studied the structure of the BF_3,FR adducts (R = methyl, ethyl, n-propyl, and isopropyl) to try to clear up the problems already referred to. Because of its dependability we have chosen the semiempirical MINDO/3 method [8] to keep the volume of computations required within reasonable limits. The BF_3,FH species serves as a test of the capacity of this method by comparing it with a more complete *ab initio* study of the potential hypersurface done on a STO-3G basis.[9]

METHODS

The geometrical optimization has been carried out by means of a variable metric minimization method using the gradient of the potential energy. This technique starts with an initial geometry q^0 in the multidimensional space of variables to be optimized, and a series of points q^n are successively generated according to formula (1) where the

$$q^{n+1} = q^n - \alpha_n A^n g^n \qquad (1)$$

determination of the constant α_n and of the matrix A^n, in each iteration, depends on the method used, and g^n is the gradient vector calculated in q^n.

The calculations were carried out using a new version [10] of the GEOMO program [11] and the MINDO/3 method [8] to calculate the energy values. Minimization of the energy can be carried out by any one of the methods proposed by Murtagh and Sargent,[12] Fletcher,[13] or Rinaldi,[14] none of which require linear minimizations for the calculation of α_n. The calculation of partial derivatives is carried out using the analytical procedure proposed by Rinaldi and Rivail.[15]

ab intio Calculations with STO-3G basis [9] have been carried out using a modified version of the GAUSSIAN-70 series of programs,[16] which uses an iterative method in geometrical optimization.

RESULTS AND DISCUSSION

The MINDO/3 potential energy hypersurface of BF_3,FH displays two minima. The two structures are shown in Figure 1. The first is open as in ref. 1. The second is a cyclic structure with strong hydrogen bond formation between two fluorine atoms, this second being 42.3 kJ mol^{-1} more stable. The appearance of this cyclic structure induced us to undertake the exploration of the STO-3G potential hypersurface in this region. The result was the appearance of a cyclic structure as a secondary energy minimum, 121.3 kJ mol^{-1} higher than the absolute minimum corresponding to the open structure.

The utilization of a semiempirical method like MINDO/3 has permitted us to carry out a more complete study than that previously done with the *ab initio* method, and to discover the existence of the cyclic structure. The relative stability of both structures depends on the method of calculation used. Optimization of the geometry by the *ab intio* calculation method which would introduce polarization functions and a correlation energy would have to be carried out to decide which of the two structures is really more stable.

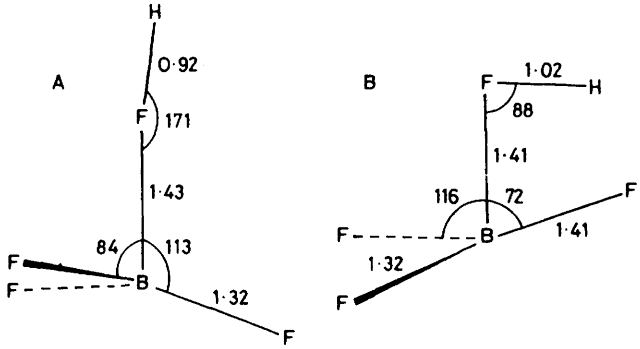

FIGURE 1 MINDO/3 stable structures of BF_3,FH

The four stable structures separated by potential barriers shown in Figure 2 were obtained for the BF_3,F-CH_3 species. The structure in Figure 2A is the least stable of the four and that in Figure 2B is 62.8 kJ mol^{-1} more stable due to the formation of an F–H bond. The structures in Figures 2C and 2D, 297.1 and 334.7 kJ mol^{-1} below that in Figure 2A, respectively, are much more stable. In both there is migration of one methyl hydrogen atom to form a strong hydrogen bond between two fluorine atoms, as in BF_3,FH.

The two stable structures shown in Figure 3 were obtained for the BF_3,FC_2H_5 adduct. Although the structure in Figure 3B is *ca.* 62.8 kJ mol^{-1} more stable than that in Figure 3A, starting from open structures the structure in Figure 3A is reached directly while a potential barrier must be surpassed for it to reach that in Figure 3B. Both structures show two rings, the pentagonal $\overline{BFCCF}$, and the tetragonal $\overline{BFHF}$, in which hydrogen forms a strong bond between two fluorine atoms, as in the preceding cases.

Three structures were found for both propyl derivatives. These structures were obtained by substituting a hydrogen atom for a methyl group in Figure 3. Two different compounds were obtained starting from the structure in Figure 3A, depending on the carbon atom the substituted hydrogen is bonded to. In both cases the energy is practically the same. Starting from the structure in Figure 3B only one species is obtained, which is 62.8 kJ mol^{-1} more stable than the preceding ones. In the case of isopropyl a further structure appears which is 217.6 kJ mol^{-1} higher in energy than the most stable one. Two identical hexagonal rings are present in which two hydrogen atoms, one from each CH_3 group, form a bond with two of the BF_3 fluorine atoms.

As we have pointed out before the same structures are obtained when passing from ethyl to propyl by substiting one hydrogen atom for a methyl group. The agreement is quantitative with reference to the values of the distances and bond angles of the rings and to the relative energies of the structures. This permits us to suppose that these structures will be maintained for higher

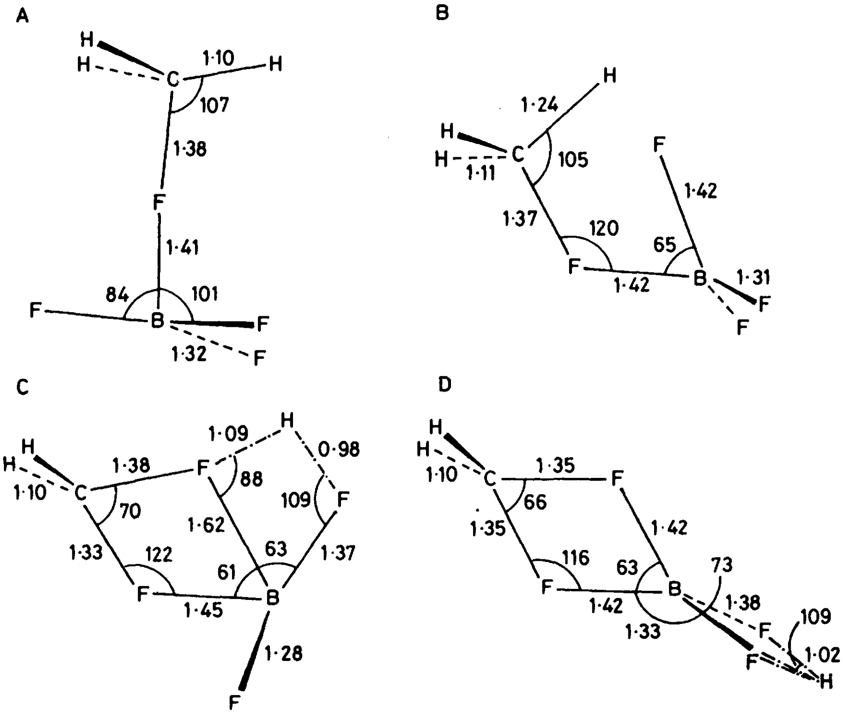

FIGURE 2 MINDO/3 stable structures of BF_3,FCH_3. — · — Represents the hydrogen bond formed by the migrated methyl hydrogen between two fluorine atoms

homologues by substiting the hydrogen atoms for the corresponding alkyl chains.

In a previous paper[1] the effect of the catalyst on FH was demonstrated by an increase of positive charge on the hydrogen atom, which went from 0.19 for the FH species to 0.28 for the BF_3,FH species, which indicates an increase in electrophilic nature. The cyclic structure we have obtained with the same method (STO-3G basis) shows a charge of 0.35 on this hydrogen. This increase in electrophilic nature is also detected for the cyclic structure by the MINDO/3 method, which gives the following values for the charge: 0.36 in the halide, 0.28 in the open structure of BF_3,FH, and 0.55 in the cyclic structure. This method affords the following values for the charge on the carbon atom in FCH_3 and for the four structures found for its adduct with BF_3: 0.51 in halide, 0.39 in the structure in Figure 2A, 0.52 in that in 2B, 0.56 in that in 2C, and 0.66 in that in 2D. However, these results do not seem very significant for the cyclic structures since the charge modifications in the rest of the electrophilic agent cannot be considered because, as in the most stable structures, part of the electrophile experiences migration. These difficulties turn out to be more evident in the rest of the series for which only cyclic structures are detected.

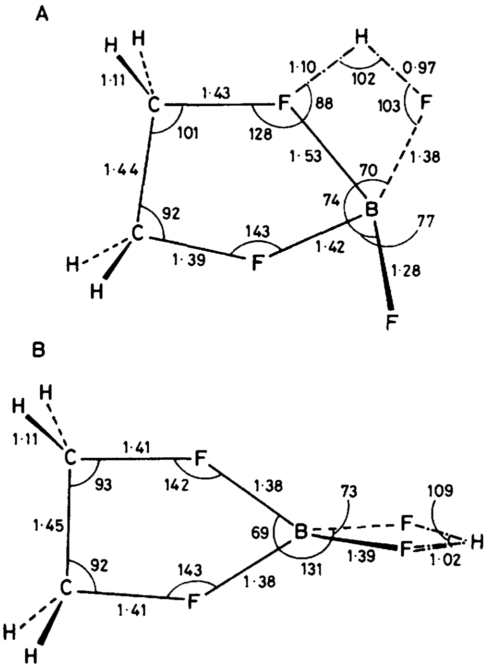

FIGURE 3 MINDO/3 stable structures of BF_3,FC_2H_5. — · — Represents the hydrogen bond formed by the migrated methyl hydrogen between two fluorine atoms

The other argument used previously[1] to interpret the role played by the catalyst is the greater effectiveness of the adduct in the heterolytic cleavage of the F–H bond to produce the corresponding ions. The values obtained through the MINDO/3 method for FH and the rest of the species studied in their most stable structure are shown in Table 1. The fact that in all cases the energy required in the adduct is much smaller can be verified.

TABLE 1

MINDO/3 energies (kJ mol^{-1}) in the heterolytic cleavage of the F–R bonds

R	$E(F^-) + E(R^+) - E(FR)$	$E(BF_4^-) + E(R^+) - E(BF_3,FR)$
H	2 846.3	1 422.2
Methyl	2 457.5	1 265.9
Ethyl	2 331.1	1 159.8
n-Propyl	2 318.6	1 169.4
Isopropyl	2 254.9	1 095.1

Another argument which was not used previously[1] is the stabilization of the LUMO going from FH to BF_3,FH (578.9 for the structure in Figure 1A and 1 128.9 kcal mol^{-1} for that in 1B in STO-3G calculations). The catalysts make the charge transfer easier and consequently increase the reactivity in orbital controlled reactions.[17] Table 2 presents the results obtained in MINDO/3 calculations. In all cases the MINDO/3 results show a stabilization of the LUMO on going from FR to BF_3,FR and for FH the same order of stabilization as in *ab intio* calculations. The LUMO of FR and BF_3,FR is antibonding between the fluorine atoms and the electrophilic centre, which means that the charge transfer favours dissociation and, on the other hand, it is enhanced by dissociation.

TABLE 2

MINDO/3 stabilization energies (kJ mol^{-1}) of LUMO going from FR to BF_3,FR species

R	A	B	C	D
H	392.1	412.8		
Methyl	258.0	207.8	66.1	79.7
Ethyl	73.3	47.6		
Isopropyl	70.3	145.3		

Perhaps the most characteristic feature of the present study is the formation of similar bicyclic structures in the adduct with FC_2H_5 and higher homologues. On the one hand the tetragonal ring, because of the stabilization provided by the hydrogen bond between the two fluorines, explains the existence of these structures as energetic minima. On the other hand the formation of the pentagonal cycle permits an interpretation of some of the isomerization phenomena. In effect, the charges on the two carbon atoms of the cycle are 0.20 and 0.26 in the structure in Figure 3A and 0.25, for both carbon atoms, in that in 3B. For the propyl derivatives the values of these charges are the same. This means that both carbon atoms have a similar electrophilic nature and therefore either will carry out the attack, explaining the presence of different isomers among the final products of Friedel–Crafts alkylation.

These cyclic adducts also permit the interpretation of the isomerization of the halogenoalkanes in the presence of Lewis acids, since the minimum energy structures in all cases show two equivalent C–F bonds, the rupture by either being possible.

Although the results obtained by the MINDO/3 method are subject to limitations,[18,19] nevertheless it seems to us that the cyclic structures found have physical reality. Cyclic structures also appeared for BF_3,FH, using the *ab initio* method, due to the tendency of hydrogen bonds to form between the fluorine atoms. Notwithstanding the fact that the relative order of energies could be altered by using other methods of calculation, the existence of energetic minima corresponding to the cyclic structures is sufficient for a certain population to exist so that they play a role in the kinetics of Friedel–Crafts catalytic alkylation.

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