Relationes

Electronic Structure of Friedel Crafts Catalysts
$BF_3 + HF$

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SCF MO LCAO calculations using two different gaussian basis sets have been performed for the species HF, F^-, BF_3, BF_4^- and HBF_4 with geometry optimization. Differences in electrophilicity and proton donating capability of HF due to the formation of the adduct with BF_3 are evidenced and discussed.

1. Introduction

The couple $HF–BF_3$ has been largely utilized for investigations on the pathway of electrophilic aromatic substitutions [1], for the determination of the basicity of aromatic hydrocarbons [2], and can be used as a model of Friedel-Crafts reactant, where the proton acts as the substituent group.

A theoretical investigation on this chemical system may be considered to be of some interest because the description of the energetic relationships between separate species and adduct as well as of the changes in electronic distribution due to the formation of the dative bond between the Lewis acid and base constitutes the preliminary step towards an interpretation of the catalysed Friedel-Crafts aromatic substitution. Several SCF MO *ab initio* calculations on BF_3 are available [3–8] but, at least as far as we know, only one *ab initio* study on BF_4^- has been published, and none on the adduct HBF_4.

In the present paper we present the results of non-empirical SCF MO investigations on nuclear geometries, energies and electron distributions of the species F^-, HF, BF_3, BF_4^- and HBF_4. Two different AO basis sets have been employed: a minimal basis where each AO is represented by three gaussians

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E. Silla *et al.*

Table 1. STO-3G geometries, energies and total atomic charges

	Geometry[a]	Energy[b]	Charge[c]
F^-		-97.6133	$q_F = -1.0$
HF	$r_{FH} = 0.956$[d]	-98.5728	$q_H = -q_F = 0.1920$
BF_3	$r_{BF} = 1.31$[e]	-318.6619	$q_B = 0.6513$ $q_F = -0.2171$
BF_4^-	$r_{BF} = 1.39$[e]	-416.6143	$q_B = 0.4899$ $q_F = -0.3725$
HBF_4[f]	$r_{BF_a} = 1.33$ $r_{BF_b} = r_{BF_c} = 1.32$ $r_{BF_d} = 1.83$ $r_{F_dH} = 0.95$ $\alpha_1 = 94$ $\alpha_2 = \alpha_3 = 97$ $\beta = 109$ $\gamma_1 = 119$ $\gamma_2 = 120$	-417.2557	$q_H = 0.2822$ $q_{F_d} = -0.1391$ $q_B = 0.6267$ $q_{F_a} = -0.2653$ $q_{F_b} = q_{F_c} = -0.2522$

[a] Bond lengths in Å, bond angles in degrees   [d] Ref. [11].
[b] Hartrees.   [e] Ref. [8].
[c] e units $= 4.803 \times 10^{-10}$ e.s.u.   [f] see Fig. 1.

(STO-3G basis set [9]) and the larger 4-31G basis having a double ζ character [6, 10].

2. Result and Discussion

Geometry optimizations with the STO-3G basis for HF, BF_3 and BF_4^- confirm what has been found by other authors using the same basis (see Table 1). For the determination of the best geometry of the adduct $BF_3 \cdot HF$ we have preliminarily imposed the constraints of keeping H on the F_aBF_d plane (see Fig. 1) and of considering the F_aBF_dH plane as a symmetry plane. The optimization of the other
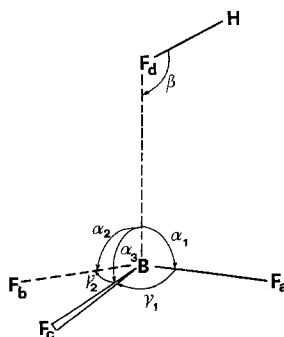
Fig. 1. Atom numbering of the adduct $HF \cdot BF_3$

8 geometrical parameters was performed iteratively, until self-consistency was reached. Finally the constraints were eliminated and it was verified that the geometrical structure corresponded to a minimum. Table 1 reports the geometries, the energies and the atomic charges we have found for the chemical species in question.

It appears evident from Table 1 that HBF_4 is actually an adduct with a relatively small stabilization energy and moderate changes in the internal geometries of the two partners. In particular in the BF_3 moiety there is only a small shift from coplanarity (the B atom is shifted 0.14 Å from the plane $F_aF_bF_c$) and a little increase of 0.01–0.02 Å in the BF bond lengths.

For the 4-31G basis we have found in the literature the geometry optimization only for HF [11]. In the search of the best geometry of BF_3 and BF_4^- we have imposed D_{3h} and T_d symmetry respectively. For HBF_4 we have limited ourselves to the optimization of the most important parameters: on the basis of the preceding STO-3G calculations we have supposed that the formation of the adduct does not alter the internal geometry of the partners, with the exception of the coplanarity of the atoms of BF_3. Consequently we have minimized the energy with respect to the distance r_{BF_d} and to the angles β and α ($\alpha_1 = \alpha_2 = \alpha_3$) (see Fig. 1). The results are reported in Table 2.

With the double ζ basis we found larger values for the bond lengths in BF_3 as well as in BF_4^-. The experimental value for BF_3 (1.31 Å [12]) shows a better accordance with the STO-3G result, while for the BF_4^- ion the B–F distance found with the 4-31G basis is practically the same as the mean value found in a set of alkaline salts (1.42_5 Å [13]). In both cases the bond lengths appear closer to reality than those obtained by means of the CNDO/2 method [14] (1.45 Å for BF_3 and 1.50 Å for BF_4^-).

In the BF_3 molecule the electron distribution of the 4-31G wavefunction corresponds to a good extent to that found by Armstrong and Perkins [3] who

Table 2. 4-31G geometries, energies and total atomic charges

	Geometry[a]	Energy[b]	Charge[c]
F^-		− 99.2478	$q_F = -1.0$
HF	$r_{FH} = 0.922$[d]	− 99.8873	$q_H = -q_F = 0.4792$
BF_3	$r_{BF} = 1.33$	− 322.7863	$q_B = 1.3219$
			$q_F = -0.4407$
BF_4^-	$r_{BF} = 1.42$	− 422.2392	$q_B = 1.3562$
			$q_F = -0.5890$
HBF_4[e]	$r_{BF_d} = 2.12$	− 422.6891	$q_H = 0.5152$
	$\beta = 126$		$q_{F_d} = -0.4632$
	$\alpha = 94$		$q_B = 1.3504$
			$q_{F_a} = -0.4755$
			$q_{F_b} = q_{F_c} = -0.4635$

[a] Bond lengths in Å, Bond angles in degrees.   [d] Ref. [11].
[b] Hartrees.   [e] See Fig. 1.
[c] e units.

used a different GTO basis set. The gross population analysis for boron ($1s^{2.00}$ $2s^{0.43}$ $2p_x^{0.47}$ $2p_y^{0.47}$ $2p_z^{0.32}$) may be quoted as an example of the concordance among the two sets of results. Consequently, the conclusions in Ref. [3] on the entity and the directions of the σ and π charge transfer are thus confirmed. In the STO-3G wavefunction the trend of charge distribution and charge transfer is similar, although the numerical values are somewhat different.

In the BF_4^- ion the largest electrophilicity of F with respect to B is evident in both wavefunctions, whereas with the STO-3G basis the occurrence of a unit negative charge in BF_4^- with respect to BF_3 produces a lowering in the positive gross charge of B passing from BF_3 to BF_4^-, with the 4-31G basis the positive gross charge of B comes out larger in BF_4^- than in BF_3. This is another example of the widely recognized tendency of the 4-31G basis to give larger bond dipoles with respect to the STO-3G one [15].

Finally, in HBF_4 the extended basis gives for the separation between the partners r_{B-F_d} and for the orientation angle β larger values with respect to those obtained with the STO-3G basis. This fact is in accord with the smaller $B-F_d$ overlap population found with the extended basis (4-31G: 0.042, STO-3G: 0.060) and with the lower stabilization energy (4-31G: 9.7 Kcal/mole, STO-3G 13.2 Kcal/mole). We may also remark that such a trend is in contrast with that found for H-bridged adducts, where STO-3G gives lower stabilization energies and higher separation distances [15].

Both basis sets give a larger positive charge on H in HBF_4 than in HF: this change in the atomic population should correspond to a larger electrophilic character of the adduct with respect to HF, at least in the first phases of the attack on a given substrate. Such a difference in electrophilicity is better evidenced in Fig. 2 where the electrostatic potential V along the F–H direction is given for both molecules. To a larger positive value of V there corresponds a larger electrophilic character.
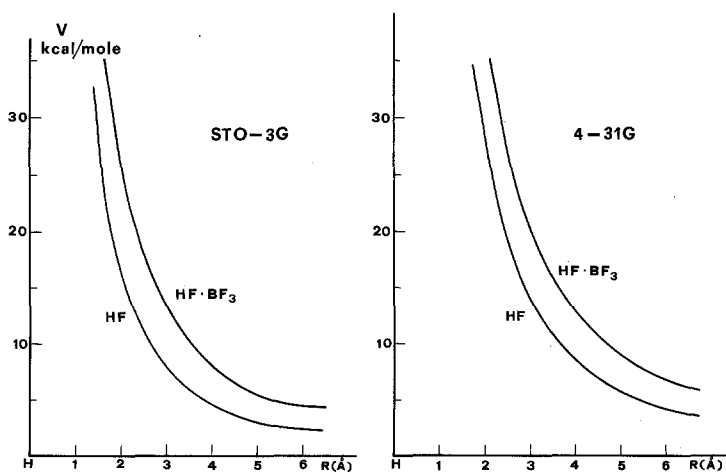

Fig. 2. Comparison of the electrostatic potential in the F–H direction for HF and FH·BF_3
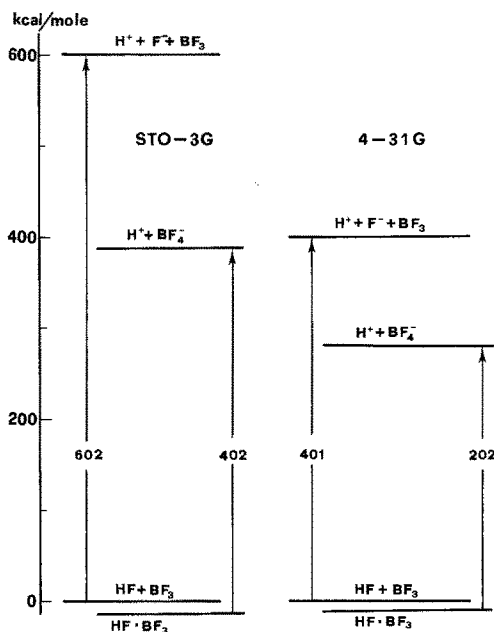
Fig. 3. Energies involved in the donation of a proton a) STO-3b, b) 4-31G

The greater effectiveness of the adduct in donating a proton is however due to energetic reasons. If one compares the two processes:

$$HF \rightarrow F^- + H^+ \tag{1}$$

$$HBF_4 \rightarrow BF_4^- + H^+ \tag{2}$$

the energy needed to release a proton is lower in reaction (2) than in reaction (1) by 119 Kcal/mole (or 200 Kcal/mole according to the STO-3G calculations see Fig. 3). The large difference between the two estimations reflects the lower quality of calculations on F^- performed with reduced basis sets at the SCF level[1], but we think that the difference in the reaction heats of the two processes can be sufficient to evidence the effectiveness of BF_3 in facilitating the transfer of H^+ from HF to aromatic substrates.

References

1. See e.g. Olah,G.A., Kuhn,S.J.: J. Am. Chem. Soc. **80**, 6635 (1958)
2. Mackor,E.L., Hofstra,A., van der Waals,J.H.: Trans. Faraday Soc. **53**, 66, 186 (1957)
3. Armstrong,D.R., Perkins,P.G.: Theoret. Chim. Acta (Berl.) **15**, 413 (1969)
4. Schwartz,M.E., Allen,L.C.: J. Am. Chem. Soc. **92**, 1466 (1970)
5. Walker,T.E.H., Horsley,J.A.: Mol. Phys. **21**, 939 (1971)
6. Hehre,W.J., Pople,J.A.: J. Chem. Phys. **56**, 4233 (1972)
7. Goutier,D., Burnelle,L.A.: Chem. Phys. Letters **18**, 460 (1973)

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[1] The affinity of BF_3 for the F^- ion has been estimated to be 71 Kcal/mole [16]: the STO-3G calculations give 213 Kcal/mole and the 4-31G ones 129 Kcal/mole.

8. Fitzpatrick,M.J.: Inorg. Nucl. Chem. Letters **9**, 965 (1973)
9. Hehre,W.J., Stewart,R.F., Pople,J.A.: J. Chem. Phys. **51**, 2657 (1969)
10. Ditchfield,R., Hehre,W.J., Curtiss,L.A., Pople,J.A.,: J. Chem. Phys **54**, 724 (1971)
11. Lathan,W.A., Hehre,W.J., Curtiss,L.A., Pople,J.A.: J. Am. Chem. Soc. **93**, 6377 (1971)
12. Kuchitsu,K., Konaka,S.: J. Chem. Phys. **45**, 4342 (1966)
13. Yeh,H.J.C., Ragle,J.C.: J. Phys. Chem. **72**, 3688 (1968)
14. Leibovici,C.: J. Mol. Struct. **14**, 459 (1972)
15. Kollman,P., McKelvey,J., Johansson,A., Rothenberg,S.: J. Am. Chem. Soc. **97**, 955 (1975)
16. Haartz,J.C., McDaniel,D.H.: J. Am. Chem. Soc. **95**, 8562 (1973)

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