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The Catalytic Effect of BF_3 on the Electrophilic Hydrogen Exchange Reaction in Benzene

An *ab initio* SCF MOLCAO Study on the Systems C_6H_6+HF and $C_6H_6+HBF_4$

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The effect of BF_3 in facilitating the reaction of hydrogen exchange in benzene under the action of HF has been evidenced by obtaining a STO-3G SCF description of the reaction coordinate in the presence and in the absence of BF_3. The catalyst reduces the height of the reaction barrier to less than half. In both cases the reaction path goes smoothly to the barrier without evidence of stable intermediates.

Key words: Electrophilic aromatic substitution mechanism – Friedel-Crafts catalysts – Aromatic complexes

1. Introduction

In a preceding paper [1] we examined the couple HF–BF_3 with particular attention to a) the changes in the electronic distribution due to the formation of a dative bond between the Lewis acid and base which can improve the proton donor ability of HF, b) the differences in the energy necessary to have a heterolytic cleavage of the H–F bond in the isolated molecule of HF and in the adduct $HF \cdot BF_3$. From these data one may infer some information on the role of the catalyst in Friedel-Crafts aromatic substitutions.

In the present paper we are going to deal with this problem in a more direct way. We shall examine, with theoretical tools, an actual case of electrophilic substitution on an aromatic substrate, namely the hydrogen exchange reaction in benzene induced by HF. Additional information on the role of catalysts in the Friedel-Crafts reaction can be gained, as it is made in the present paper, by examining the differences in the

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mechanism of proton addition and subtraction to C_6H_6 by HF in the absence or in the presence of BF_3. The investigation will be centered on the portion of the reaction path near the top of the barrier separating reagents and products. We shall carefully investigate if such an intermediate geometry corresponds to a stable σ intermediate (i.e. if there is a local minimum on the potential surface). The catalytic effect of BF_3 will be measured by the lowering it produces on the reaction barrier height.

All calculations have been performed in the SCF MOLCAO formalism using the minimal STO-3G basis set [2].

2. Results and Discussion

The identification of the actual features of a reaction mechanism is a hard task even if performed at a low level of accuracy. In the present case, having a model composed only of one molecule of substrate and one of reagent, as the first step in this identification one should calculate significant portions of the potential energy surface describing 36 internal degrees of freedom in the C_6H_6+HF case and 48 when BF_3 is also taken into consideration. A simplification is necessary and we have resorted to a set of approximations, increasing at each stage the number of degrees of freedom explicitly taken into consideration.

The first, more drastic, approximation (Appr. I) reduces the dimensionality of the problem to two. It consists in considering the molecular conformation of the system near the top of the barrier separating reagents and products as representable by an adduct $C_6H_7 \cdot X$, where X stands for F or BF_4 [1]. At this level of approximation the geometry of $C_6H_7^+$ has been taken from a paper of J. Hehre and J. A. Pople [3], while the geometry of BF_4^- has been taken from Ref. [1]. C_6H_7 has a C_{2v} symmetry, with five CH groups still retaining the conformation they have in benzene, while the CH_2 group is perpendicular to the ring,with a $H_1\hat{C}_1H_2$ angle ($\alpha=\alpha_1+\alpha_2$) of 105.3° and a C_1–H distance of 1.106 Å (see Fig. 1). By keeping rigid the geometry of the partners we have explored the potential energy sheet corresponding to motions of X in the plane perpendicular to the ring and containing the CH_2 group. Fig. 2 gives the potential energy map for the case X=F.

Such a figure requires some observations. The constraint of keeping unaltered the C_{2v} symmetry of the C_6H_7 portion can be acceptable, even if as a first approximation, only in a portion of space smaller than one reported in Fig. 2 and centered in the vicinity of the C_2 axis. The large minima in the direction of the two C–H bonds are evidently affected by the restrictions we have imposed. It is interesting however to remark that there is not a relative minimum in correspondence with the location of F on the symmetry axis of C_6H_7F complex along the minimum energy path. A provisional definition of a portion of the reaction

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[1] We have not put formal charges on the partners of the adduct because they are somewhat misleading. In fact, as it will be shown later, in general the charge separation between partners is far from being equal to 1.

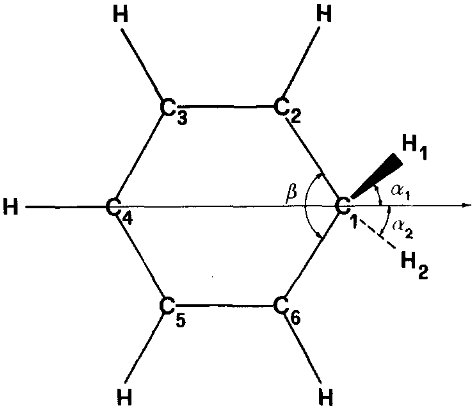
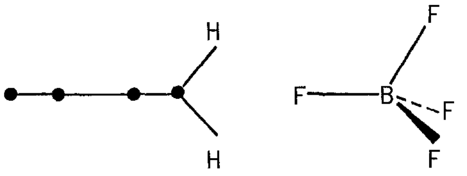


Fig. 1. Atom numbering and coordinates in the C_6H_7 moiety of the C_6H_7X complexes. The following parameters have been kept constant in all the calculations: $R_{C_1C_2}=1.472$ Å, $R_{C_2C_3}=R_{C_3C_4}=1.40$ Å, $R_{C_2H}=1.094$ Å, $R_{C_3H}=R_{C_4H}=1.08$ Å, $\beta=110.9°$, $H\hat{C}_2C_3=118.3°$, $H\hat{C}_3C_4=H\hat{C}_4C_3=120°$

coordinate can be obtained from Fig. 2. It is given by means of a dashed line on the same figure. The energy profile along this portion of the reaction coordinate, as well as along the orthogonal coordinate passing through the saddle point and going in the C_4–C_1 axis direction, is given in Fig. 3[2].

When one applies the same approximation to the case where $X=BF_4$ one should add three other degrees of freedom corresponding to the rotations of BF_4 around its gravity center. The calculations are more complex but the essential results are easily reported. Two different conformations should be the best candidates for the reaction intermediate: in the first one (I) the bonding is supported by one F atom only, while in the second (II) there are two separate bonds, each concerning a different H–F couple. It turns out that the reaction path leads to conformation II and that conformation I is less stable in the whole region of space corresponding to the reaction intermediate (see Fig. 4). As it is possible to see by examining Fig. 2 there is no energy barrier for the decomposition of the complex along the reaction coordinate, but the energy profile is decidedly flatter than in the C_6H_7F case.



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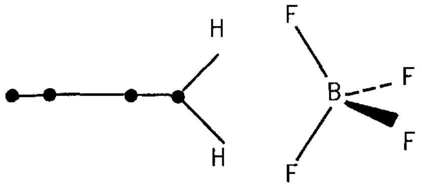

II

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[2] We do not report here the energy curve for the third coordinate, orthogonal to the plane of Fig. 2. This curve too confirms that the point on the symmetry axis is a saddle point.

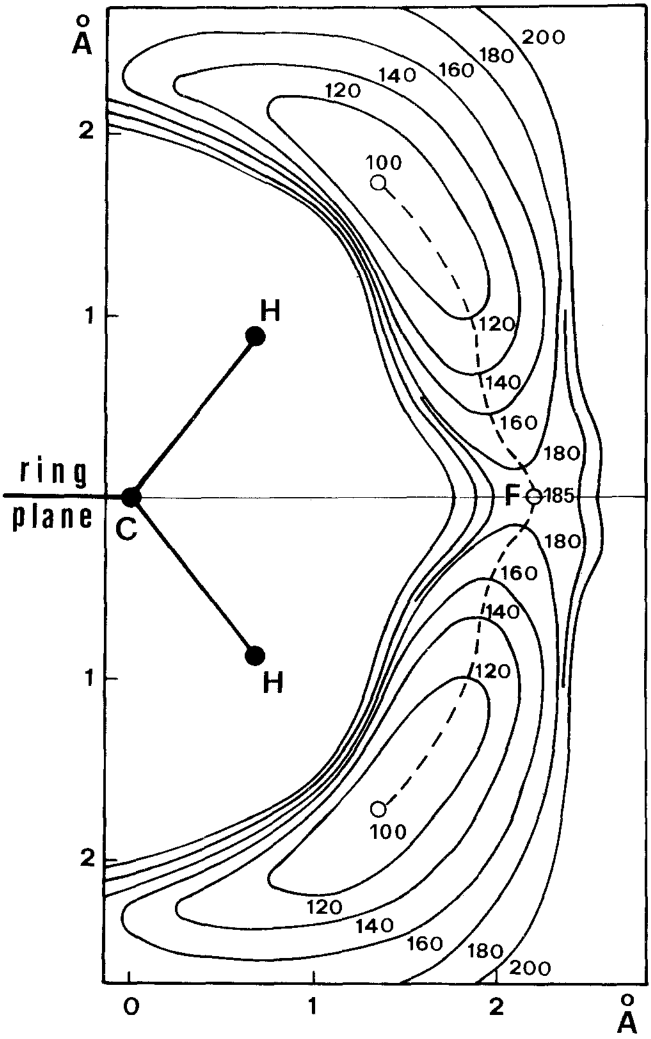


Fig. 2. Total energy map for the displacement of F in the C_6H_7F complex. The map refers to the symmetry plane orthogonal to the carbon ring and has been obtained by keeping rigid the geometry of the C_6H_7 moiety (Approximation I). The energy curves are given in kcal/mole with respect to a zero corresponding to the energy of the separate reagents (C_6H_6 and HF). The reaction coordinate is given as a dashed line

From the values of the energies of the reactants and of the intermediates given in Tables 1 and 2 one can measure the effect BF_3 has in lowering the barrier height for the H exchange reaction. In fact in the first case the energy difference between separate reagents and transition state is 185.0 kcal/mole ($E(C_6H_7 \cdot F - E(C_6H_6) - E(HF))$ and in the second one 75.0 kcal/mole ($E(C_6H_7 \cdot BF_4) - E(C_6H_6) - E(HBF_4))$.

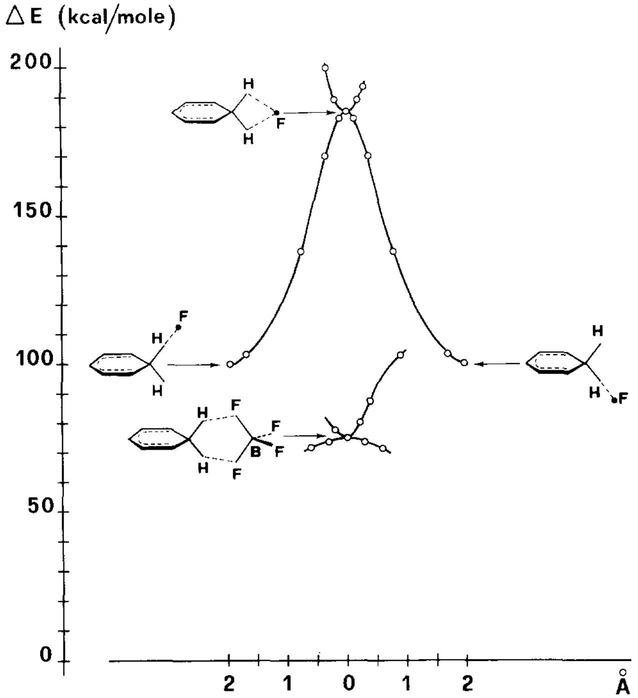


Fig. 3. Energy profile along a portion of the reaction coordinate for the hydrogen exchange in C_6H_6+HF and $C_6H_6+HF+BF_3$ (Approximation I). The definition of the reaction path for the reaction in the presence of the catalyst has been obtained by means of a map similar to that reported in Fig. 2. In addition is reported the energy profile for the coordinate orthogonal to the reaction path and passing through the saddle point, along the C_4–C_1 axis

The picture of the intermediate complex is distorted by the constraints introduced in the preceding calculations. A somewhat more refined description is given by approximation II, in which we have considered a 6-dimensional subspace, including also the distances R_{CH_1}, R_{CH_2} and the angles α_1 and α_2 among the parameters under variation. By recalculating a map like that of Fig. 2 (with optimization of the other four parameters for each position of F) it is confirmed that there is no energy barrier for the decomposition of C_6H_7F. The geometry of the transition state greatly changes with respect to the previous calculations (the results are reported in Table 2) and its energy is lowered to 123.2 kcal/mole above that of the separate reagents. The energy profile along the reaction coordinate is much sharper than in the previous approximation.

A similar investigation on the $C_6H_7BF_4$ system leads to analogous results: there is no energy barrier for the decomposition of the transition state even if the parameters α_1, α_2, R_{CH_1}, R_{CH_2} are separately optimized along the reaction path. In this approximation the reaction barrier height decreases to 55.7 kcal/mole (confor-

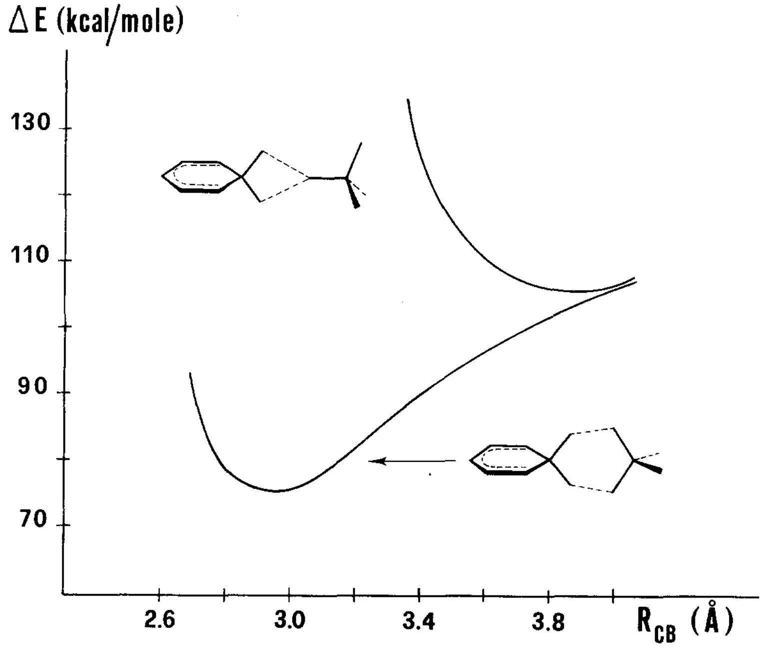


Fig. 4. Comparison of the energy trends for displacements along the C_4–C_1 axis of the BF_4 moiety of $C_6H_7BF_4$ in the two conformations I and II (Approximation I)

mation II). The catalytic effect is represented by a difference of 67.5 kcal/mole in the relative heights of the two barriers.

The next step in the series of subsequent approximations should involve a relaxation of the internal geometry of the BF_4 moiety. If one optimizes in $C_6H_7BF_4$ also the BF distances for the two F atoms involved in the bond, one finds only moderate gains in the energy: the barrier height decreases to 52.8 kcal/mole. For a further control we have performed an analogous optimization on structures of type I: the energy difference between the two conformations is larger than in approximation I (see Table 2 where the best values for both conformations are reported). We have not gone on relaxing other coordinates of the BF_4 moiety because the balance between

Table 1. STO-3G geometries and energies of the separated species

	Geometry[a]	Energy[b]
F^-		−97.6133
HF	$r_{HF}=0.956$	−98.5728[c]
BF_3	$r_{BF}=1.31$	−318.6619[d]
BF_4^-	$r_{BF}=1.39$	−416.6143[d]
HBF_4	see Ref. [1]	−417.2557[e]
C_6H_6	$r_{CC}=1.40$ $r_{CH}=1.08$	−227.8901[f]

[a] Bond lengths in Å. [b] Hartrees

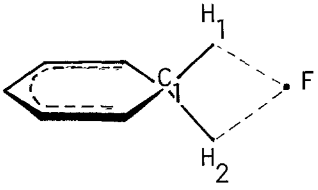
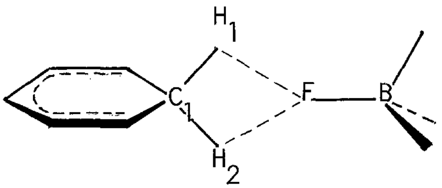
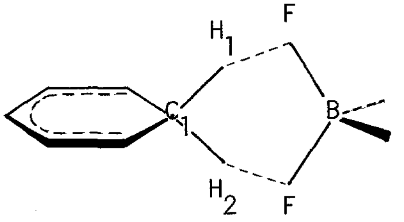
[c] Lathan, W. A., Hehre, W. J., Curtiss, L. A., Pople, J. A.: J. Am. Chem. Soc. **93**, 6377 (1971)

[d] Fitzpatrick, M. J.: Inorg. Nucl. Chem. Letters **9**, 965 (1973)

[e] Ref. [1]

[f] Hehre, W. J., Radom, L., Pople, J. A.: J. Am. Chem. Soc. **94**, 1496 (1972)

Table 2. Energies[a] and geometries[b] of the C_6H_7X species in the different approximations

		Approx. I	Approx. II
	$r_{C_1H_1}$	1.106	1.40
	$r_{C_1H_2}$	1.106	1.40
	$H_1\hat{C}_1H_2$	105.3	64
	r_{HF}	1.764	1.176
	r_{CF}	2.20	2.10
	E	−326.1681	−326.2665
	$r_{C_1H_1}$	1.106	1.110
	$r_{C_1H_2}$	1.106	1.110
	$H_1\hat{C}_1H_2$	105.3	92
	r_{HF}	2.011	1.832
	r_{BF}	1.390	1.420[c]
	r_{CB}	3.870	3.830
	E	−644.9785	−644.9821
	$r_{C_1H_1}$	1.106	1.240
	$r_{C_1H_2}$	1.106	1.240
	$H_1\hat{C}_1H_2$	105.3	84
	r_{HF}	1.498	1.272
	r_{BF}	1.390	1.450[c]
	r_{CB}	2.950	2.980
	E	−645.0263	−645.0617

[a] Hartrees

[b] Bond lengths in Å. Angles in degrees. The values of the other geometrical parameters are given in Fig. 1

[c] The optimization concerns only the BF bonds directly involved in the formation of the complex, the others being kept at 1.39 Å

computer costs and additional information one may gain in this way seems to be unfavourable[3]. A graphical representation of the changes in the energy barriers in going from approximation I to this stage of approximation II is given in Fig. 5.

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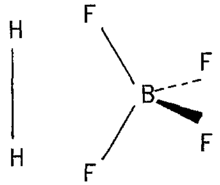
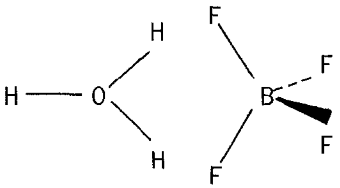
[3] Additional information on the lowering of the barrier height due to a complete optimization of the internal geometry of BF_4 can be inferred from calculation on the electrically neutral model systems



III



IV

having both R_{HH} equal to $R_{H_1H_2}$ in C_6H_7 and R_{HF} equal to the analogous distance in $C_6H_7BF_4$. An optimization of the $F\hat{B}F$ angles and of the other two BF distances produces a lowering of the energy of less than 4 kcal/mole.

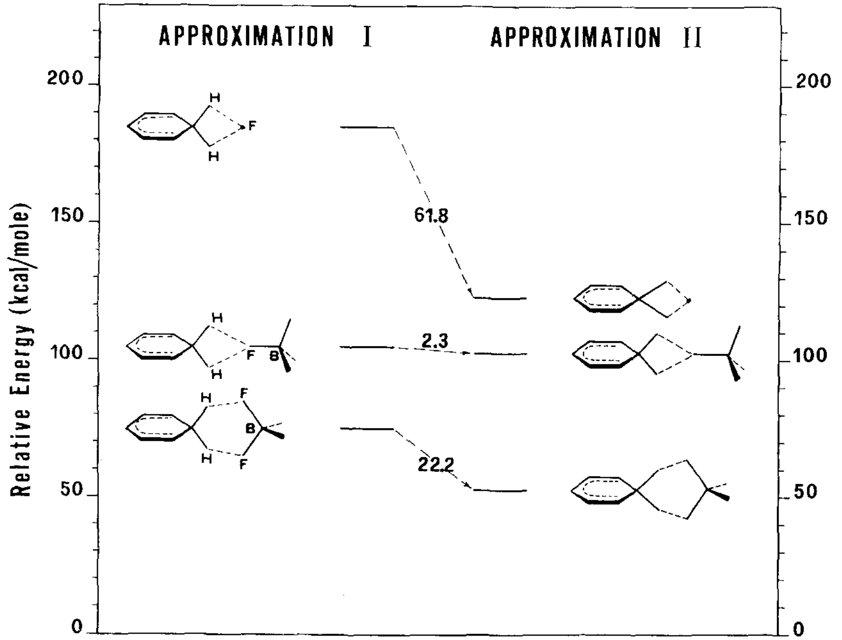


Fig. 5. A comparison of the energy barriers in the two approximations employed in this paper

A third step in the series of successive approximations should involve a relaxation of the internal geometry of the carbon ring. It is easy to see that changes of the barrier heights due to the relaxation of the carbon ring are modest. From calculations on benzene at distorted geometries one may estimate that variations in β (the most important parameter not optimized in the preceding calculations) can produce lowerings of only a few kcal/mole in this barrier height. For example if one passes from regular benzene to a distorted molecule C_6H_6 having $\beta=110.9°$ and $\alpha_1=52.65°$, there is a rising of the internal energy of 45.5 kcal/mole, only a tenth of which is due to the change in β: so it is reasonable to suppose that the optimization of this angle will produce changes of only a fraction of this energy.

In conclusion the energy barrier for the hydrogen exchange in benzene induced by HF turns out to be of the order of 120 kcal/mole, and the catalytic effect of BF_3 in lowering this barrier is of the order of 70 kcal/mole.

Such values refer to the STO-3G SCF approximation and suffer from the limitations of such crude calculations. The greatest error is due to the use of a minimal basis set in the SCF calculations. If one takes as a test the calculations on the heterolytic cleavage of the HF bond in HF and in HBF_4 performed in parallel with STO-3G and 4-31G basis sets [1] one finds that the minimal basis set largely overestimates the energy required in this process. In the present case there is not a complete dissociation with fragments at infinite separation and the errors will be presumably of a lesser entity. Calculations on the models III and IV performed in parallel with the two basis sets may suggest the prevision, we report here only to give a rough idea of the order of magnitude of the effect, that the use of the 4-31G basis set should produce a lowering of about the 25% of the barriers[4]. Failing to consider the other effects, though themselves interesting, like the change of the correlation energy in going from separate reagents to the transition state, one should produce errors of an order of magnitude decidedly lower than the effects discussed in this paper.

The greater effectiveness of HBF_4 with respect to HF in releasing a proton, evidenced in Ref. [1], is confirmed by the analysis of the charge distribution of the intermediates C_6H_7F and $C_6H_7BF_4$ (conformation II). In C_6H_7F the H–F distance is relatively short, the net charge on F is only $-0.196\,e$ ($-0.192\,e$ in hydrogen fluoride), the H–F bonds still maintain a noticeable covalent character (the overlap population for each H–F bond is $-0.212\,e$). $C_6H_7BF_4$ is characterized by the occurrence of a six-membered ring involving two separate H–F interactions. Such steric disposition reduces the compression of the CH_2 group. The covalent character of the H–F bond is lower than in the preceding case (the overlap population is $-0.174\,e$) and the charge on BF_4 is $-0.524\,e$[5].

We have so far concentrated our attention on the regions of the energy hypersurfaces corresponding to the transition states. Such investigation is sufficient to point out the effect of the catalyst, but it will be of some interest to add a few other details on the stages of the reaction preceding the intermediate complex.

It was anticipated before that the reaction path in approximation II is steeper than that given in Fig. 2. In fact the occurrence of an intermediate $C_6H_7\cdot F$ having appreciable interaction with two hydrogens is restricted to a quite narrow region and displacements of F even of less than 0.1 Å from the C_2 axis lead to structures corresponding to a distorted benzene perturbed by a HF molecule not too stretched with respect to the free molecule (R_{HF} is in the range 1.05–1.03 Å).

The approach of HF from infinity gives rise to small attractive interactions in a large region. The largest stabilization energy seems to occur when HF points to the middle of the ring, but there is not a great difference from other approaches. A more detailed description of such π hydrogen-bonded adducts is not very interesting to understand the mechanism of the reaction. In fact the information we have reported is sufficient to show that the present calculations and the experimental evidence agree (see however Ref. [4]) in supporting a mechanism which is characterized by the occurrence of a σ complex [5]. The only feature which does not correspond to the generally accepted picture is the absence of a barrier stabilizing the intermediate complex.

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[4] In addition one should remember that the 4-31G basis set, though superior to the minimal one in giving previsions of energy differences, is not sufficiently large to give correct previsions. For example the value of the energy necessary for the heterolytic cleavage of HF reported in [1] is still in error of about 30 kcal/mole.

[5] The charge separation between C_6H_7 and F is surely underestimated in the STO-3G SCF calculations, but there are no reasons to suppose that the trend of the charge separations in the two transition states will be reversed if one passes to more accurate calculations.

Also for the reaction in the presence of BF_3 the intermediate has a structure clearly corresponding to a σ complex. The information we have on the preceding stage of the reaction is just sufficient to state that there is no barrier on the reaction path immediately preceding the formation of the complex. The region of space where both hydrogens are directly involved in the interaction seems to be larger than in the C_6H_7F case and going on along the reaction coordinate there is a rotation of BF_4 which therefore remains linked to one H atom only. Further investigations concerning the early stages of the approach of HBF_4 to C_6H_6 have not been performed. Presumably (see Ref. [1]) the π-bonded adducts will have a somewhat larger stabilization energy in the HF case. On this topic one should remember that there is not general agreement (compare Refs. [6] and [7]) on the problem if HBF_4 can exist as a free acid in anhydrous hydrogen fluoride (as to the experimental conditions employed, see e.g. the classical studies of Olah and Kuhn [8]). In order to investigate this subject one should introduce a significant portion of the liquid into the model and treat the system with other techniques. The approach we have adopted cannot in this case go further than the study of the intermediate and of the consequences the catalyst has on its structure and energy.

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