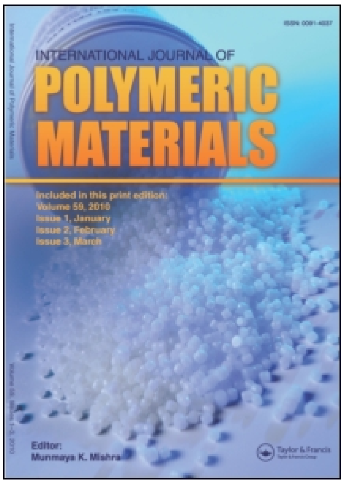

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Theoretical Estimation of Acid Strength of Fluorine Hydrogen – Boron Fluoride Complexes

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The calculation of complexes $R_nBF_{3-n} \cdot HF$ (there is $R = CH_3$ and C_2H_5) has been carried out by the quantum-chemical semi-empirical MNDO method in Dewar and Teel parameterization. The geometrical and electronic structure of these complexes was obtained. On an example of simple H-acids we estimated their acid strength. We found that irrespective of the ligand surrounding of *B* atom the complexes $R_nBF_{3-n} \cdot HF$ have rather high acid strength ($pK_\alpha = -17.9 - 14.9$).

Keywords: Hydrogen Fluorine; Boron Fluoride; complexes; acid strength; theoretical calculations

AIMS AND BACKGROUND

The theoretical methods for estimating the acid strength of H-acids are important in establishing the acid strength role in various chemical processes because it is often difficult to estimate the acid strength by experiment because the corresponding reliable indicators are absent. This is particularly relevant for H-complexes of $R_nBF_{3-n} \cdot HF$ type that sometimes require considerable time for preparation and

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identification. In this connection the theoretical methods of estimating the acid strength of H-acid and H-complexes represent doubtless interest. In the first time such method has been offered in [1] through calculation by quantum-chemical CNDO/2 method in Santry-Pople-Segal parametrization [2] of the maximum electronic charge on hydrogen atom of simple H-acids and H-complexes – q_{H+}^{max} and which according [3–7] correlates with values of universal acidity index (pK_a) represented by the linear dependence: $pK_a = 45.256 - 193.577$ (q_{H+}^{max}) [1].

It was therefore interesting to carry out quantum-chemical calculations of acid strength parameters of H-complexes by other semi-empirical methods, in particular, by MNDO in Dewar and Teel parameterization [8]. On modern computers of a class IBM PC Pentium with work frequency ~200 MHz the calculations of these models (molecules with number orbitals about 50) is practically executed in a few minutes with optimization of geometric structure of all parameters, that may have a role in the "fast-method" estimation of acid strength of H-acids and H-complexes.

The aim of this study was to carry out the quantum-chemical calculation of H-complexes of fluorine hydrogen–boron fluorides by MNDO method and the estimation their acid strength.

METHODOLOGY

To calculate the mentioned models of H-acids we used MNDO method in Dewar and Teel parameterization, that describes very well the repulsion of non-divided electronic pairs. The minimization of total energy of the system has been performed at all geometric parameters by Davidon-Flatcher-Powell method [8]. This method gives very precise value of valent angles and gives more accurate sequence of levels of molecular orbitals than other methods. Initial models of H-acids and complexes $R_nBF_{3-n} \cdot HF$ are characterized by the number of atoms from 2 to 24, by amount of orbitals from 2 to 51, by the total charge, which is equal to zero for all molecular systems. Furthermore, when proton is separated to infinity $\sum q_{sys} = -1$ and the multiplicity is $M = 2S + 1$ (where S is summary spin of molecules in basic condition is equal to zero). Therefore $M = 1$ as is the case with other models. The calculation has been performed in classical approximation of isolated molecule in a gas phase.

RESULTS AND DISCUSSION

We first established by MNDO method (Tabs. I, II) the correlation dependences of q_{H+}^{max} – the maximum values of electronic charge on hydrogen atom, ΔE^{H+} – the energy of proton isolation and pK_a – the universal acidity index for the most simple typical H-acid calculated by MNDO method.

The regressive analysis has allowed us to establish the following correlation dependences with the value of pK_a, q_{H+}^{max} and ΔE^{H+}, here

TABLE I Quantum-chemical parameters of some H-acids. ($\sum q_{sys} = 0$, where q_{sys} is total charge of system)

H-acid	E_0, *kJ/mole*	E_F, *kJ/mole*	E_E, *kJ/mole*	*PI*, *kJ/mole*	q_{H+}^{max}	pK_a[3, 9]
C_2H_5OH	– 64075	– 263	– 169309	+1089	0.18	18
CH_3OH	– 48974	– 240	– 104176	+1101	0.18	16
CH_4	– 17861	– 50	– 37497	+1338	– 0.17	42
H_2	– 2729	+ 3	– 4191	+1518	0.0	45
H_2O	– 33912	– 255	– 48295	+1176	0.16	15.7
HF	– 47695	– 250	– 55666	+1430	0.28	0
NH_4^+	– 24800	+689	– 49987	+2489	0.23	9.5

E_0 – total energy of system; E_F – formation energy; E_E – total electronic energy of system; *PI* – potential of ionization.

TABLE II Quantum-chemical characteristics of some H-acids without extracting their proton to infinity. ($\sum q_{sys} = -1$, where q_{sys} is total charge of system)

Model	E_0, *kJ/mole*	E_F, *kJ/mole*	E_E, *kJ/mole*	*PI*, *kJ/mole*	ΔE^{H+}, *kJ/mole*
$C_2H_5O^-$	– 62634	– 190	– 159258	+237	– 1441
CH_3O^-	– 47533	– 166	– 92883	+232	– 1441
CH_3^-	– 16206	– 238	– 30108	– 116	– 1655
H^-	– 1057	– 309	– 1057	– 90	– 1672
HO^-	– 32313	– 24	– 39146	– 45	– 1599
F^-	– 46150	– 72	– 46150	+150	– 1545
NH_3	–	–	–	–	– 651

$\Delta E^{H+}_{M(H2)} = E_{0M\,(H2)} - E_{0\,M(H2)}$ (The calculation ΔE^{H+} for remaining models of H-acids has been executed similarly).

(R is coefficient of correlation):

1. $pK_\alpha = 42.11 - 147.18(q_{\mathrm{H+}}^{\max}), \quad R = 0.99(\mathrm{I})$

2. $pK_\alpha = -1025 - 0.021(\Delta E), \quad R = 0.46(\mathrm{I})$

$$pK_\alpha = 121.36 + 0.249(\Delta E) + 1.189(\Delta E)^2, \quad R = 0.73(\mathrm{II})$$

$$pK_\alpha = -3313.03 - 9.458(\Delta E) - 0.0081(\Delta E)^2 - 2.1903 \cdot 10^{-6}(\Delta E)^3, \quad R = 0.98(\mathrm{III})$$

These data show that the ratio (1) represents already in first approximation the functional dependence with $R = 0.96$, and the ratio (2) becomes satisfactory only in third approximation. Therefore the ratio (1) is more suitable for use in estimation of acid strength of H-acids. The remaining quantum-chemical parameters (E_0, E_F, E_E, PI) do not give satisfactory correlation dependences with pK_a. Consequently the ratio (1) of $pK_a = 42.11 - 147.18(q_{\mathrm{H+}}^{\max})$ has been applied by us to estimate pK_a of H-complexes $R_nBF_{3-n} \cdot HF$.

Data of quantum-chemical calculations of fluorine hydrogen – boron fluorides are complexes presented in Tables III and IV. The optimal geometric and electronic structure of these complexes was also obtained. The bond lengths are equal to: $R_{\mathrm{BF}} = 0.136\,\mathrm{nm}$, $R_{\mathrm{HF}} = 0.096\,\mathrm{nm}$, $R_{\mathrm{BF1}} = 0.152\,\mathrm{nm}$, $R_{\mathrm{BC}} = 0.163\,\mathrm{nm}$, $R_{\mathrm{CC}} = 0.153\,\mathrm{nm}$, $R_{\mathrm{CH}} = 0.11\,\mathrm{nm}$. The valent angles are close to tetrahedral (Fig. 1).

TABLE III The total energy of molecular system (E_0), potential of ionization (PI), dipole moment (D), electronic charges on atoms (q) and universal acidity index (pK_a) for models of complexes $R_nBF_{3-n} \cdot HF$ (where $R = CH_3$)

No.	*Model*	E_0, *kJ/mole*	*PI, kJ/mole*	*D, dB*	q_B	q_F	q_{H+}^{max}	pK_a
1.	$BF_3 \cdot HF$	– 163988.16	1406.496	6.29	+0.455	– 0.063	+0.408	– 17.9
2.	$BF_2CH_3 \cdot HF$	– 163988.16	1150.506	6.16	+0.230	– 0.060	+0.397	– 17.9
3.	$BF(CH_3)_2 \cdot HF$	– 133989.03	1024.926	5.52	+0.026	– 0.029	+0.389	– 16.3
4.	$B(CH_3)_3 \cdot HF$	– 104004.39	1032.654	5.12	– 0.206	+0.013	+0.387	– 15.1

TABLE IV The total energy of molecular system (E_0), potential of ionization (PI), dipole moment (D), electronic charges on atoms (q) and universal acidity index (pK_a) for models of complexes $R_nBF_{3-n} \cdot HF$ (where $R = CH_3$)

No.	*Model*	E_0, *kJ/mole*	*PI, kJ/mole*	*D, dB*	q_B	q_F	q_{H+}^{max}	pK_a
1.	$BF_2C_2H_5 \cdot HF$	– 179096.40	1112.832	6.06	+0.247	– 0.066	+0.401	– 16.9
2.	$BF(C_2H_5)_2 \cdot HF$	– 164207.44	1002.708	5.27	+0.054	– 0.028	+0.390	– 15.3
3.	$B(C_2H_5)_3 \cdot HF$	– 149338.77	1009.470	4.72	– 0.158	+ 0.136	+0.389	– 15.1

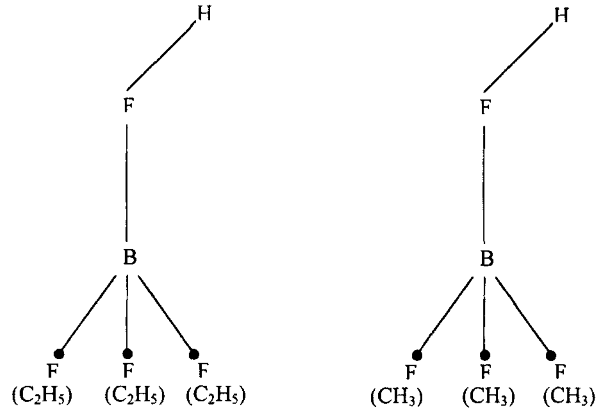

FIGURE 1 Geometric and electronic structure of $R_nBF_{3-n} \cdot HF$ complexes (where $R = CH_3, C_2H_5$).

The evidence of existance of complexes based on boron fluorides and HF is their high negative values of total energy of complexes $E_0 = (-179096{,}40 \div -104004{,}39)$ kJ/mole.

The electronic charge on B atom essentially depends on ligand environment that in sequence

$$BF_3 \cdot HF, B(CH_3)F_2 \cdot HF, B(CH_3)_2F \cdot HF, B(CH_3)_3 \cdot HF$$

and

$$BF_3 \cdot HF, B(C_2H_5)F_2 \cdot HF, B(C_2H_5)_2F \cdot HF, B(C_2H_5)_3 \cdot HF$$

decreases from $+0.455$ to -0.206, while the charge on F atom of protondonor HF increases from -0.063 to $+0.136$.

The charge on hydrogen atom of promotor HF practically does not depend on ligand environment of B atom and is falls in the range of $+0.40 \pm 0.01$. In accordance with ratio (1) for $R_nBF_{3-n} \cdot HF$ (where $R = C_2H_5$) $pK_a = -16.9 \div -15.1$, this reflects their high acid strength [9].

These data agree with the estimation of acid strength of fluorine hydrogen-boron fluorides complexes by the CNDO/2 method [6, 7].

CONCLUSIONS

Thus, quantum-chemical calculation of models of complexes $R_nBF_{3-n}\cdot HF$ (where R = CH_3, C_2H_5) by classical semi-empiric MNDO method in Dewar and Teel parameterization with optimization of geometry of all parameters by Davidon-Flatcher-Pawell method allowed us to find their optimal geometric and electronic structure. To estimate the acid strength of these complexes we used the MNDO method to calculate the maximum electronic charge on hydrogen atom ($q_{H+}^{\max}$) and the ratio $pK_a = 42.11 - 147.18(q_{H+}^{\max})$. It was shown, that irrespective of ligand surrounding of *B* heteroatom the complexes $R_nBF_{3-n}\cdot HF$ possess rather high acid strength $pK_a = -17.9 \div -14.9$.

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