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Quantum-Chemical Study of Various Pathways to Carbenium Ions from Olefins and Alkyl Fluorides in the Medium of Hydrofluoric Acid

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Abstract—Elementary reactions of carbenium ion generation from olefins and alkyl fluorides in the medium of hydrofluoric acid are studied by the Hartree–Fock method taking into account electron correlation at the MP2 level and by the DFT (B3LYP) method in the 6-31++G** basis set. Based on enthalpies calculated for these reactions, possible pathways to carbenium ions in the olefin–HF system are determined. A conclusion is drawn that carbenium ions can be formed from olefins by protonation and from the corresponding alkyl fluorides and their protonated forms. It is shown that the heterolytic decomposition of alkyl fluoride in the medium of liquid HF is possible due to the stabilization of carbenium and fluoride ions by hydrogen bonds with HF molecules. The discrete model of microsolvation and the polarizable continuum model (PCM) are used to estimate a decrease in the activation barrier of the heterolytic decomposition of alkyl fluorides due to solvation in the medium of liquid hydrofluoric acid.

INTRODUCTION

Acid-catalyzed olefin conversions in the presence of sulfuric and hydrofluoric acids are traditionally considered as classic examples of carbenium-ion reactions. The foundations of the current theory of carbenium-ion mechanisms of acid-catalyzed hydrocarbon conversions were developed in [1–3] proceeding from the stoichiometry and composition of reaction products. Data obtained for the olefin–sulfuric acid system fill an important place in the cited works. According to the experimental data, in the reaction of olefins with H_2SO_4 or HF, alkyl sulfates or alkyl fluorides are first formed [4–9]. Nevertheless, the classic scheme of acid-catalyzed olefin polymerization usually includes the following elementary steps: chain initiation by the formation of carbenium ions via olefin protonation; chain growth with various secondary reactions and rearrangements, which accompany carbenium-ion polymerization; and chain termination by intramolecular hydride transfer from olefin molecules [10, 11]. The choice of an acid determines the lifetime and reactivity of aliphatic carbenium ions. Convincing evidence for that was found in the studies of H–D exchange in isobutane for D_2SO_4 [12], DF/SbF_5 or FSO_3D/SbF_5 [13]. A systematic ^{13}C NMR study of olefin transformations in sulfuric acid has begun recently [14, 15]. However, attempts to detect aliphatic carbenium ions in these systems by spectroscopy were unsuccessful [16]. This indicates that carbenium ions can exist as very unstable species in very low equilibrium concentrations. On the other hand, aliphatic carbenium ions were observed using high-pressure mass spectrometry [17–20]. Therefore, it was interesting to carry out an *ab initio* quantum-chemical study of the states of the simplest carbenium ions in the media of H_2SO_4 and HF using modern models of solvation.

Earlier, we carried out quantum-chemical calculations of neutral and protonated forms of some monoalkyl sulfates, and their complexes with one H_2SO_4 molecule [21, 22]. However, because the monoalkyl sulfate + nH_2SO_4 complexes were difficult to calculate, the alternative pathway to carbenium ions from neutral alkyl sulfates by their heterolytic dissociation has not been studied theoretically. Obviously, without correct description of the solvent effect on the process of charge separation in the heterolytic dissociation of alkyls sulfates, correct calculation of the activation energy is impossible either. Therefore, we turned to a theoretical study of acid-catalyzed olefin conversions in hydrofluoric acid. In this case, the solvent effect can be taken into account within a framework of the microsolvation model with the aid of continuum models since an HF molecule has few electrons.

This work deals with quantum-chemical calculations of possible pathways to carbenium ions in the olefin + hydrofluoric acid system and thermodynamic and activation parameters of the corresponding elementary steps. To take into account the solvent effect, we use both the discrete model of microsolvation and a combination of the discrete and continuum models. In this work, we restrict ourselves to considering some simpler olefins (propylene and isobutylene) and the corresponding alkyl fluorides.

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CALCULATION METHOD

The full geometry optimization of the structures under study was carried out within the framework of the Hartree–Fock method taking into account the electron correlation at the second-order Müller–Plesset perturbation theory (MP2) level using the 6-31G** and 6-31++G** basis sets. To speed up geometry optimization for molecular species in the MP2 calculation in the 6-31++G** basis set, we used geometry calculated at the MP2 level for the 6-31G** basis set. When estimating the reaction enthalpies, we used absolute energies calculated at the MP2 level for the 6-31++G** basis set. This made it possible to partially reduce the error associated with the basis set incompleteness. In addition, geometry optimization for some structures was carried out by the DFT B3LYP method [23, 24] using the 6-31G** and 6-31++G** basis sets. The geometry was optimized using analytical gradients without taking into account point-group symmetry. To characterize stationary points on potential energy surfaces obtained at the stage of geometry optimization, we calculated the matrix of force constants and analyzed normal vibrations. The calculation of the electrostatic component of the free energy of solvation was carried out in the framework of polarizable continuum model (PCM) [25]. Quantum-chemical calculations were carried out using the programs GAMESS [26], Gaussian 94 [27] and Gaussian 98 [28] and SGI Power Challenge and Pentium II (300 MHz) computers.

RESULTS AND DISCUSSION

Anhydrous hydrofluoric acid is known to dissociate to a very small degree, and the formation of solvated protons or $[HFH]^+$ ions by protolysis in liquid HF is possible in very small concentrations [29]. Therefore, along with commonly known pathway to carbenium ions in olefin protonation by the reaction

$$R^1R^2C{=}CR^3R^4 + [HFH]^+ \longrightarrow R^1R^2CH{-}C^+R^3R^4 + HF, \quad \text{(Ia)}$$

it is reasonable to consider other pathways as well. First of all, we should consider the interaction of olefins with nondissociated hydrofluoric acid:

$$R^1R^2C{=}CR^3R^4 + HF \longrightarrow R^1R^2CH{-}C^+R^3R^4 + F^-, \quad \text{(Ib)}$$

and the reaction with alkyl fluorides

$$R{-}F + [HFH]^+ \longrightarrow R^+ + [FH\ldots FH], \quad \text{(IIa)}$$

$$R{-}F + HF \longrightarrow R^+ + [FHF]^-. \quad \text{(IIb)}$$

To estimate the enthalpies of reactions (Ia), (Ib), (IIa), and (IIb) in the gas phase, we carried out *ab initio* quantum-chemical calculations of the absolute energies E of the above-mentioned alkenes, corresponding alkyl fluorides, carbenium ions, monomeric and dimeric HF, $[HFH]^+$, $[FHF]^-$, and F^-. These calculations were carried out by the Hartree–Fock method with MP2 electron correlation. Furthermore, we calculated the electrostatic component of the free energy of solvation ΔG_{el} for charged species using the PCM model, according to which the solvent is characterized by the dielectric permittivity of HF ($\varepsilon = 84$) [30]. In addition, the energies of the above structures were calculated by DFT (B3LYP) in the 6-31G** and 6-31++G** basis sets.

Based on the calculated values of energies shown in Table 1, it is possible to calculate the enthalpies of reactions (Ia), (Ib), (IIa), and (IIb) in the gas phase, which are listed in Table 2. Analysis of the ΔH_r values suggest that gas-phase reactions (Ib) and (IIb) accompanied by charge separation are highly endothermic. The enthalpy of reaction (Ib) is 25 kcal/mol higher than the enthalpy of reaction (IIb). This result is probably due to the experimentally proven fact that the addition of an HF molecule to a double C=C bond occurs in two steps. Initially, the π-complex is formed [31], which then transforms into alkyl fluoride via an asymmetric transition state (*cis*-addition). Using data from Table 1, it is easy to calculate the enthalpies of HF addition to propene and isobutene (–14.1 and –16.1 kcal/mol, respectively). Although these reactions are exothermic, the corresponding calculated activation energies in the gas phase are 42.1 and 38.5 kcal/mol (MP2/6-31++G** calculation). In the case of *trans*-addition of the HF molecule, a minimum appears on the potential energy surface that corresponds to an energetically unfavorable intermediate species. Earlier, it has been suggested that *trans*-addition is facilitated if the two elementary steps in the solution (proton transfer from one HF molecule and the addition of fluoride ion from another HF molecule) occur synchronously [32]. However, if olefin is protonated by the $[HFH]^+$ species (reaction (Ia)), the formation of the corresponding carbenium ion is very exothermic because of a substantial difference in proton affinities of HF and the olefin molecules [33].

Taking into account the ionic nature of the reactions under consideration, we expected a strong effect of a polar solvent (liquid HF) on the thermodynamic parameters. Indeed, the PCM estimates of enthalpies for reactions (Ia), (Ib), (IIa) and (IIb) in liquid HF (Table 2) point to substantial changes in the energetics of reactions (Ib) and (IIb). They become less endothermic and therefore thermodynamically more probable. Thus, the *trans*-addition of HF to a double bond in the olefin is highly probable in liquid HF in the case of reaction (Ib). In contrast, the effect of liquid HF on reactions (Ia) and (IIa) results in a substantial decrease in the reaction heat as calculated within the framework of the PCM model. This is due to a strong difference in the solvation of balky carbenium ions (ΔG_{el} = 57.2 kcal/mol for *tert*-Bu^+) and the proton donor $[HFH]^+$ (ΔG_{el} = 94.6 kcal/mol). Nevertheless, the above reactions are more exothermic than reactions (Ib) and (IIb). Note that, according to the calculated values shown in Table 2, alkyl fluorides can also be a source of carbe-

Table 1. Absolute energies of molecules and ions (*E*, a.u.) and zero-point energies (*ZPE*, kcal/mol) calculated by the Hartree–Fock (HF) method taking into account electron correlation at the MP2 level and by the DFT (B3LYP) method in the 6-31G** basis set (calculations in the 6-31++G** basis set are presented in parentheses)

	E(HF)	*E*(MP2)	*E*(B3LYP)	*ZPE*(MP2)
iso-C_4H_8	–156.1238463	–156.6919245	–157.2388343	69.7
		(–156.7007575)	(–157.2455370)	
tert-$C_4H_9^+$	–156.4584626	–157.0097177	–157.5675923	75.2
		(–157.0132293)	(–157.5687038)	
tert-BuF	–256.1733861	–256.9293145	–257.7103375	80.2
		(–256.9495223)	(–257.7273115)	
C_3H_6	–117.0816141	–117.5039139	–117.9165481	51.4
		(–117.5113730)	(–117.9228771)	
iso-$C_3H_7^+$	–117.3937560	–117.7996698	–118.2225282	56.8
		(–117.8020165)	(–118.2230607)	
iso-PrF	–217.1302679	–217.7389630	–218.3878770	62.3
		(–217.7576459)	(–218.4045410)	
HF	–100.0116908	–100.1946391	–100.4274616	6.0
	(–100.0243123)	(–100.2159193)	(–100.4513906)	
HF…HF	–200.0329032	–200.4016566	–200.8699203	14.0
	(–200.0555439)	(–200.4397418)	(–200.9041736)	13.6
$[HFH]^+$	–100.2151813	–100.4021205	–100.6369823	12.2
	(–100.2167618)	(–100.4064010)	(–100.6415964)	
$[FHF]^-$	–199.4532576	–199.8235475	–200.2899904	
	(–199.5105647)	(–199.9120848)	(–200.3867538)	6.7
F^-	–99.3504820	–99.5266066	–99.7540888	
	(–99.4185864)	(–99.6238467)	(–99.8596980)	–

Table 2. Enthalpies of reactions (ΔH_r, kcal/mol) in the gas phase (g) and liquid HF (l) calculated by the MP2/6-31++G** method and the differences between the reactant and product energies (ΔE, kcal/mol) calculated by MP2 and B3LYP/6-31++G** method for the elementary reaction of carbenium ion formation from alkenes and alkyl fluorides in the course of protonation by HF and $[HFH]^+$ in the gas phase

Reaction	ΔH_r		ΔE	
	E(MP2) + *ZPE*		MP2	B3LYP
	g	l		
$(CH_3)_2C{=}CH_2 + HF \longrightarrow (CH_3)_3C^+ + F^-$	174.9	5.0	175.4	168.5
$(CH_3)_2C{=}CH_2 + [HFH]^+ \longrightarrow (CH_3)_3C^+ + HF$	–77.2	–39.8	–76.5	–83.4
$(CH_3)_3CF + HF \longrightarrow (CH_3)_3C^+ + [FHF]^-$	146.4	16.1	150.7	140.1
$(CH_3)_3CF + [HFH]^+ \longrightarrow (CH_3)_3C^+ + [HF…HF]$	–64.1	–26.7	–60.9	–65.2
$(CH_3)HC{=}CH_2 + HF \longrightarrow (CH_3)_2HC^+ + F^-$	189.1		189.7	182.9
$(CH_3)HC{=}CH_2 + [HFH]^+ \longrightarrow (CH_3)_2HC^+ + HF$	–63.1		–62.3	–69.0
$(CH_3)_2HCF + HF \longrightarrow (CH_3)_2HC^+ + [FHF]^-$	158.5		163.3	154.4
$(CH_3)_2HCF + [HFH]^+ \longrightarrow (CH_3)_2HC^+ + [HF…HF]$	–52.0		–48.3	–50.9

nium ions in liquid HF. Thus, our *ab initio* PCM calculations show that the classic scheme of carbenium ion generation with proton can be viewed as a rough approximation of real processes that occur in the acid.

Let us consider reactions of carbenium ion generation with the participation of alkyl fluorides in more detail. Table 2 shows that the process of proton transfer from $[HFH]^+$ to alkyl fluoride with further carbenium ion generation (reaction (IIa)) is noticeably less exothermic than in the case of olefin. We carried out full geometry optimization using the MP2 method for the $RF\cdot\cdot[HFH]^+$ complex, where R = *tert*-Bu and *iso*-Pr. In the case of isopropyl fluoride, the C–F bond is very long (1.7 vs. 1.39 Å). On the potential energy surface of the [*tert*-Bu–F··$[HFH]^+$] complex, we found no minimum that corresponds to the complex with a hydrogen bond. Rather, we only found a minimum that corresponds to the ion–molecular complex (*tert*-Bu^+ + FH··FH) with a distance between the C^+ and F atoms of about 2.4 Å and with an as long FH··FH hydrogen bond as 1.62 Å. As can be seen from Table 2, the DFT (B3LYP) calculation quantitatively agrees with the calculation by the MP2 method. Thus, if the proton donor is $[HFH]^+$, both isobutylene and the corresponding alkyl fluoride give the carbenium ion, which is stabilized by solvation in liquid HF.

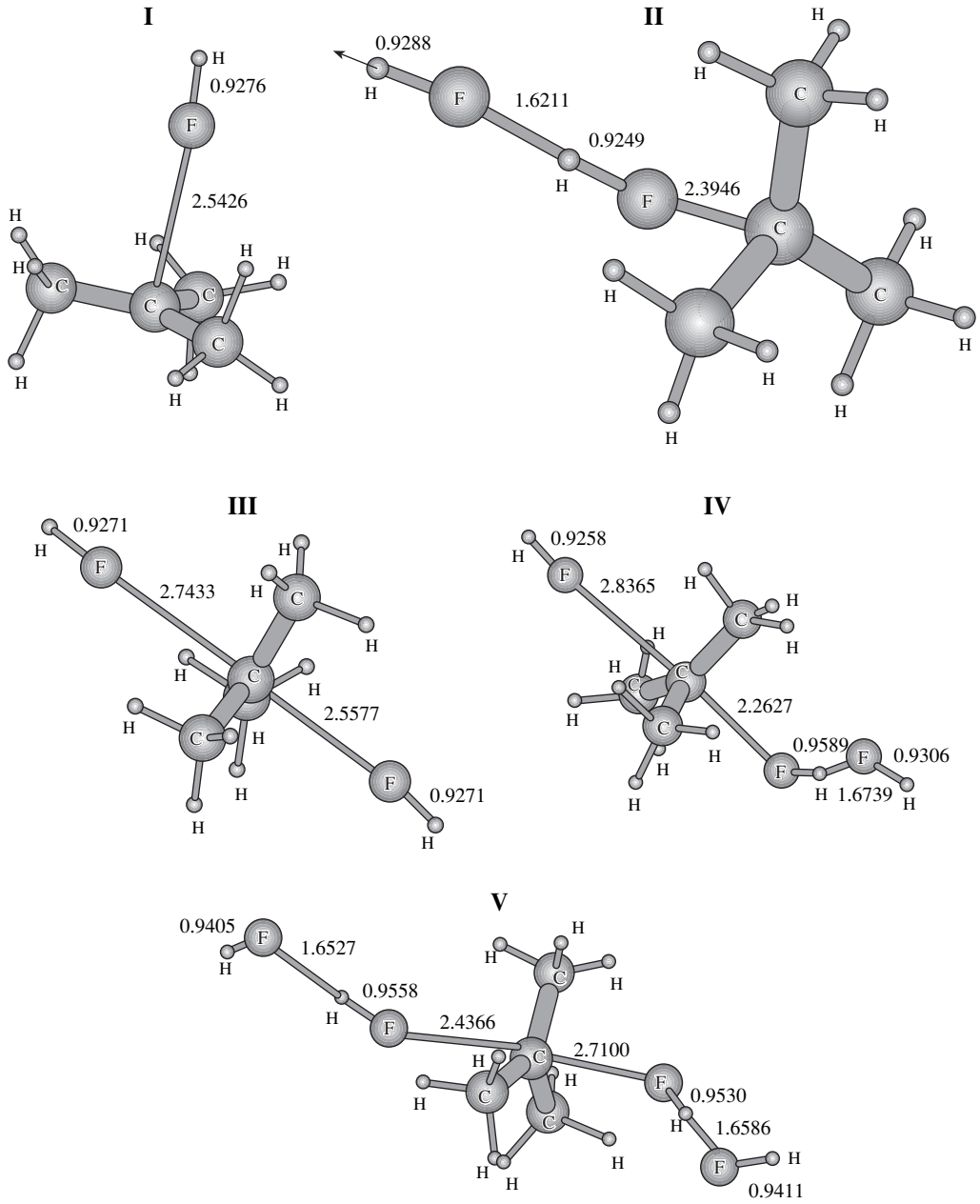
To estimate the stabilization energy of the *tert*-Bu^+ ion in the medium of liquid HF, we carried out *ab initio* Hartree–Fock calculations taking into account electron correlation at the MP2 level for a number of solvate complexes of *tert*-Bu^+ with one to four HF molecules. The structures of solvate complexes are shown in the figure with the calculated distances between HF molecules and with distances between the central carbon atom of *tert*-Bu^+ and HF molecules in the first solvate shell of the carbenium ion. The absolute energies of solvate complexes are shown in Table 3. The calculated data suggest that the contributions from separate HF molecules to the complexation energy ΔE are nearly additive: 12–13 kcal/mol per HF molecule (see Table 4). Note that, according to the calculated ΔE values in the case of the *tert*-Bu^+ complex with two HF molecules, their asymmetric arrangement relative to the *tert*-Bu^+ ion (structure **II**) is more favorable (by 1.7 kcal/mol). The vacant *p*-orbital on one side relative to a plane that passes through four carbon atoms is accessible to reactants. The activation barriers to the abstraction of one HF molecule from the complex $[HF\cdot\cdot(CH_3)_3C^+\cdot\cdot FH\cdot\cdot FH]$ or two HF molecules from the complex $[FH\cdot\cdot HF\cdot\cdot(CH_3)_3C^+\cdot\cdot FH\cdot\cdot FH]$ with the formation of the above-mentioned $[(CH_3)_3C^+\cdot\cdot FH\cdot\cdot FH]$ complex are 13.2 and 17.3 kcal/mol, respectively. Moreover, the estimates of activation energies change insignificantly when the electrostatic component of the solvation free energy of these ion–molecular complexes is taken into account. For the latter complex, the free energy of solvation varies within 50–54 kcal/mol. If we additionally take into account the energy of broken hydrogen bonds [34–36], e.g. ~28.3 kcal/mol (MP2/6-31++G** calculation) in the cyclic tetramer $(HF)_4$, then it can be seen that the formation of the complex of *tert*-Bu^+ with HF results in its moderate stabilization while preserving significantly electrophilic nature of the cation [37] and its reactivity. This is evident from the Mulliken charges at the central carbon atom and the HOMO energy for the complexes under consideration (Table 4). Interestingly, that despite the flow of charge density (from 0.04 to 0.20 a.u.) from the coordinated HF molecules onto the *tert*-Bu^+ ion, the positive charge on the central carbon atom in the complexes somewhat increases. Thus, according to our *ab initio* calculations that takes into account electron correlation and the effect of microsolvation, the carbenium ion $(CH_3)_3C^+$ in the medium of liquid HF exists for a finite time until reactant molecules such as olefin or isobutane, which have a pronounced affinity to carbenium ion, enter the solvate shell.

It is known that the concentration of $[HFH]^+$ species in liquid HF is lower than 10^{-6} mol/l [38]. Therefore, it is interesting to consider an alternative pathway to *tert*-Bu^+ via heterolytic dissociation (IIb), which is highly endothermic because the strong carbon–fluorine bond [39]. According to MP2/6-31++G** calculation, the heterolytic dissociation of the carbon–fluorine bond in *tert*-BuF in the gas phase requires 196.06 kcal/mol. Obviously, the heterolytic dissociation of *tert*-BuF in liquid HF should be much less endothermic because of solvation of the fluoride ion and *tert*-Bu^+ with HF molecules.

Earlier, the method of ion cyclotron resonance showed that the fluoride ion and the HF molecule forms the $[FHF]^-$ complex with a very strong hydrogen bond

Table 3. Absolute energies of ion–molecular complexes (*E*, a.u.) calculated by the Hartree–Fock (HF) method taking into account electron correlation at the MP2 level in the 6–31G** basis set

Complex		*E*(HF)	*E*(MP2)
$(CH_3)_3C^+$…FH	I	–256.4854929	–257.2239049
$(CH_3)_3C^+$…FH…FH	II	–356.5135878	–357.4396945
HF…$(CH_3)_3C^+$…FH	III	–356.5158700	–357.4369457
HF…$(CH_3)_3C^+$…FH…FH	IV	–456.5425248	–457.6554089
FH…HF…$(CH_3)_3C^+$…FH…FH	V	–556.5701542	–557.8689046



Structures of solvate complexes $(CH_3)_3C^+FH$ (**I**), $(CH_3)_3C^+FHFH$ (**II**), $HF(CH_3)_3C^+FH$ (**III**), $HF(CH_3)_3C^+FHFH$ (**IV**), and $HFHF(CH_3)_3C^+FHFH$ (**V**). The distances of HF molecules, from the C^+ atoms and HF molecules are given in angstroms.

[40, 41]: for $E[HF(g) + F^-(g) \longrightarrow FHF^-(g)]$, a value of 39 ± 1 kcal/mol was obtained. The calculation of the ΔG_{el} value for the fluoride ion complex with one HF molecule according to the PCM (MP2/6-31++G**) method (Table 5) gives a value of –73.1 kcal/mol. Analogous calculation for the [*tert*-$Bu^+\cdots FH$] complex gives –53.9 kcal/mol (see Table 4). As a result, the consideration of solvation within the framework of the combined PCM model and microsolvation of the fluoride ion and *tert*-Bu^+ by one HF molecule with a correction for the energy of two broken hydrogen $FH\cdots FH$ bonds leads to a decrease in the energy of heterolytic dissociation of the C–F bond in *tert*-BuF to 34 kcal/mol. Thus, even one HF molecule in the solvate shell of the fluoride ion and *tert*-Bu^+ results in a substantial decrease in the energy of the heterolytic dissociation of the carbon–fluorine bond in *tert*-butyl fluoride (from 196 to 34 kcal/mol).

To estimate more precisely the energy of fluoride ion solvation in the medium of liquid HF, we carried out *ab initio* calculation using the Hartree–Fock method with electron correlation at the MP2 level for anion F^- complexes with different numbers HF molecules. The absolute energies of complexes are shown in

Table 4. The energies of complex formation (ΔE), solvation (ΔG_{el}, kcal/mol), and frontier orbitals (E_{HOMO} and E_{LUMO}, a.u.); Mulliken charges (a.u.) for the central carbon atom in the *tert*-butyl cation; the overall charge q(HF) for the coordinated HF molecules

Complex	E_{HOMO}	E_{LUMO}	q(C)	q(HF)	ΔE	ΔG_{el}
$(CH_3)_3C^+$	–0.7333	–0.1526	0.259	–	–	–57.2
$(CH_3)_3C^+$…FH	–0.7162	–0.1272	0.271	0.042	–12.3	–53.9
$(CH_3)_3C^+$…FH…FH	–0.7047	–0.1117	0.277	0.065	–25.5	–53.2
HF…$(CH_3)_3C^+$…FH	–0.6974	–0.1061	0.284	0.080	–23.8	–50.5
HF…$(CH_3)_3C^+$…FH…FH	–0.6832	–0.0646	0.232	0.204	–38.8	–50.8
FH…HF…$(CH_3)_3C^+$…FH…FH	–0.6803	–0.0829	0.260	0.144	–50.6	–50.9

Table 5. Absolute energies of the complexes of fluoride ion with HF molecules (E, a.u.), the energies of complex formation (ΔE, kcal/mol) calculated by the Hartree–Fock method taking into account electron correlation at the MP2/6-31++G** level, and the ΔG_{el} energies (kcal/mol)

Complex	E(HF)	ΔE	E(MP2)	ΔE	ΔG_{el}(HF)	ΔG_{el}(MP2)
$[FHF]^-$	–199.5105647	–42.5	–199.9120848	–45.4	–76.9	–73.1
$[FHFHF]^-$	–299.5803520	–70.8	–300.1750053	–74.9	–64.7	–59.8
$[F(HF)_3]^-$	–399.6402755	–93.3	–400.4276017	–97.9	–56.9	–52.6
$[F(HF)_4]^-$	–499.6903224	–109.5	–500.6699779	–114.5	–53.0	–47.4
$[F(HF)_6]^-$	–699.7616432	–123.7	–701.1261116	–129.7	–50.6	–43.2

Table 5. The analysis of obtained data points to strong nonadditivity of HF molecule contributions to the complex-formation energy. This fact agrees with the results of calculation by the Hartree–Fock method in the extended basis [42]. The estimates of F^- and *tert*-Bu^+ solvation energies enabled us to calculate the enthalpy of the heterolytic C–F bond dissociation in *tert*-BuF in the medium of hydrofluoric acid. If we restrict ourselves to considering only the first solvation shell and introduce a correction for the energy of one hydrogen bond breaking in liquid HF, which is equal to 8 kcal/mol [34], then the contributions of microsolvation for the fluoride ion solvated by four HF molecules and for *tert*-Bu^+ solvated by two HF molecules are (114.5 – 32) = 82.5 and (23.8 – 16) = 7.8 kcal/mol, respectively (see Tables 4 and 5). Note that when two additional molecules are added to the first solvate shell of the fluoride ion, the contribution of microsolvation changes only slightly and becomes 129.7 – 48 = 81.7 kcal/mol. Within the framework of the PCM model, the contributions of the rest of the medium (liquid HF^-) to the solvation of $[F(HF)_4]^-$ and $[HF\cdot\cdot(CH_3)_3C^+\cdot\cdot FH]$ are 47.4 and 50.5 kcal/mol, respectively. Thus, the combined (microsolvation + continuum PCM model) allowed us to obtain a value of 188.2 kcal/mol for the energy of $(CH_3)_3C^+$ and F^- solvation in liquid HF. Therefore, within the framework of the combined model of solvation, the enthalpy of heterolytic C–F dissociation in *tert*-BuF in the medium of liquid HF is ~8 kcal/mol. The gas-phase and liquid-phase enthalpies of the heterolytic dissociation of the C–F bond in *tert*-BuF (196 and 8 kcal/mol, respectively) indicate that the solvent has a tremendous effect on the reaction probability. According to the data obtained in this work, the heterolytic dissociation of the C–F bond in *tert*-BuF with carbenium ion formation is possible in liquid hydrofluoric acid, and the rate of this reaction would depend on the height of the activation barrier. Taking into account that the transition state is strongly polarized in similar reactions with charge separation, one may expect that the activation barrier to fluoride ion abstraction is substantially lowered in liquid HF. Indeed, the B3LYP calculation in the 6-31++G** basis set for the $[(CH_3)_3C^+[FHF]^-]$ complex with the R(C–F) distance varied with a 0.2 Å step enabled us to estimate the height of this barrier as 30 kcal/mol. Earlier, it has been shown for a similar reaction of *tert*-butyl chloride decomposition in water that the solvent decreases the activation barrier to 20 kcal/mol [43, 44].

Thus, the carbenium ion *tert*-Bu^+ can be formed by isobutene or *tert*-BuF protonation by the $[HFH]^+$ species or by the heterolytic dissociation of *tert*-BuF if solvation by HF molecules takes place in the liquid phase. In the first case, the reaction rate will be limited by a very low concentration of $[HFH]^+$ species, because after *tert*-BuF protonation, the carbenium ion is formed without an activation barrier. In the second case, the activation barrier of heterolytic carbon–fluorine bond dissociation is rather high, and the rate constant of this reaction is rather low. This reaction is noticeably endothermic in liquid HF. Therefore, the contribution of this pathway to the formation of the carbenium ion *tert*-Bu^+ is probably comparable with the contribution of the former one.

Conclusions of this work can be refined by a more correct account of the energy of F^- ion solvation. We plan to do that in future.

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