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A Theoretical Investigation on the Role of Solvent in Solvolytic Reactions

VI. An *ab initio* MO Calculation for Dissociation of Fluoromethane in Hydrofluoric Acid

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The dissociation curve of fluoromethane in hydrofluoric acid was calculated by an *ab initio* SCF MO technique using the minimal STO-3G basis set. The model of the solvent includes eleven HF molecules, simulating the first solvation shell. The position of these molecules was borrowed from a previous semiempirical calculation. A preliminary *ab initio* study of solvation of CH_3^+ and F^+ in H_2O and HF justifies this assumption.

Key words: Dissociation of fluoromethane – *ab initio* MO calculations – Model solvation in HF.

1. Introduction

In the course of a theoretical investigation on the mechanism of solvolytic reactions, the dissociation of fluoromethane was throughly investigated [1–4] by means of semiempirical calculations at the CNDO/2 level of approximation [5]. Solvents showing different polarity, polarizability and dielectric constant were considered and the model, which describes the solvent effect through the behaviour of the first solvation shell, allows a satisfactory description of the reaction intermediates. In particular it is noteworthy that the dissociation process in water and in hydrofluoric acid is different from that in methane. In the former solvents dissociation occurs after formation of different kinds of ion pairs [2, 3], unlike in methane, where fluoromethane dissociates without previous association of the solvated counterions [4]. Moreover, the geometries optimized at each point (r) of the dissociative path, allow to visualize the structure of tight (contact) and loose (solvent separated) ion pairs.

One of the drawbacks of our model is the use of a semiempirical technique throughout the calculations. This choice was due both to the dimensions of the solvated systems taken into consideration, where $9 \sim 12$ solvent units were employed to describe the first solvation shell, and to the consequent number of geometrical variables, necessary to describe the dissociative process adequately.

In the present paper a study of the dissociation of fluoromethane in solution by *ab initio* MO calculations at STO-3G basis set level is presented. Hydrofluoric acid was chosen as solvent since it is the smallest high dipole solvent with large dielectric constant taken into consideration in previous calculations [3]. Moreover, the solvation of CH_3^+ and F^- ions in water and hydrofluoric acid were widely investigated by *ab initio* calculations using STO-3G and 4-31G basis sets.

Our goal was to confirm through non-empirical calculations the existence in solution of the ion pairs predicted by semiempirical methods, as well to offer more accurate information on the geometries of the solvated ions, to be used as reference for semiempirical calculations.

Solute/solvent interaction energy was evaluated in the framework of different basis sets, and in the case of STO-3G calculations the basis set superposition error (BSSE) was corrected by means of the counterpoise method [6, 7].

The assumptions included in the solvent model and the related limitations, discussed previously, are available in Refs. [1–4].

2. Calculations

Standard *ab initio* LCAO–SCF MO calculations for the systems CH_3F, HF, H_2O, $F^-(HF)_n$ ($n = 0$–6), $F^-(H_2O)_n$ ($n = 0$–6), $CH_3^+(HF)_5$, $CH_3^+(H_2O)_5$, and $CH_3F(HF)_{11}$, were carried out by the GAUSSIAN-70 method [8]. Minimal STO-3G and split-valence 4-31G basis sets were employed. The charge distributions were computed following the Mulliken approach [9].

The total energy of the solvated fluorine anion in water and hydrofluoric acid was evaluated assuming different numbers of solvent molecules to describe the first solvation shell.

The geometries of the first solvation shell of F^- and CH_3^+ were optimized by keeping the solvent molecules rigid and optimizing both the position and the orientation of each solvent unit. The adopted symmetry constraints were retained throughout the calculations. The geometries for each considered system are shown in Fig. 1. The geometries of the solvent units and of CH_3^+, optimized by STO-3G and 4-31G basis sets, were taken from Ref. [10] and are collected in Table 1.

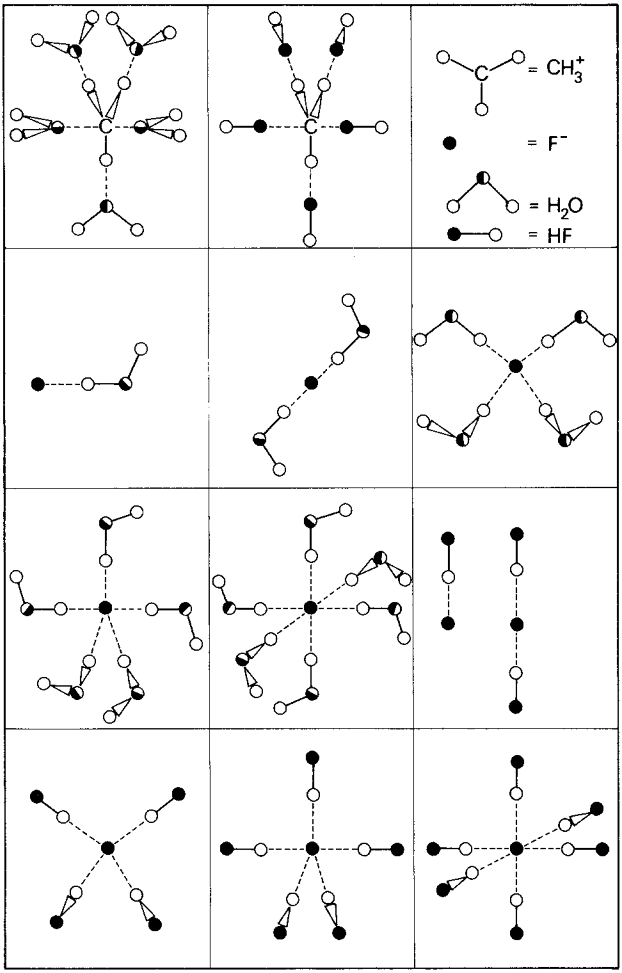

Fig. 1 Geometries of the systems $CH_3^+(s)_5$ and $F^-(s)_n$, with $n = 1$–6 and $s = H_2O$ and HF.

The *ab initio* dissociation path of fluoromethane in solution is a cumbersome problem with respect to the computational time. To keep the calculations at a reasonable level, the solvent units (HF) were retained at positions optimized by previous CNDO/2 calculations [3], at each value of the dissociation coordinate *r*.

We note that the study of a molecular system at a fixed geometry by a computational technique superior to that used to optimize the geometry itself, is a standard procedure; e.g. 4-31G basis set was used in energy computations with a geometry optimized with a minimal STO-3G basis set [11]. Moreover, we think that the study of fluoromethane dissociation in solution by *ab initio* MO calculations not including configuration interaction is appropriate, since we calculate in reality the change of conformational energy of a super-molecule. Such a situation is

Table 1. *Ab initio* (STO-3G and 4-31G) energies, geometries, and charges for F^- and CH_3^+ ions in gas phase and in solution ($s = H_2O$, HF)

System	*a*	STO-3G	4-31G	System	*a*	STO-3G	4-31G
$CH_3^+(H_2O)_5$	$-E$ (a.u.)	413.81708	418.89544	$CH_3^+(HF)_5$	$-E$ (a.u.)	531.77317	533.73322
	R(H–O_{eq})	1.83	2.14		R(H–F_{eq})	1.71(1.52)^c	1.95
	R(C–O)$_{ax}$)	1.86	2.06		R(C–F_{ax})	1.81(1.66)	2.13
	Q(C)	+0.04	−0.15		Q(C)	+0.06	−0.15
	$Q(H_{CH_3})$	+0.18	+0.30		$Q(H_{CH_3})$	+0.20	+0.32
	$Q(H_{eq})$	+0.19	+0.42		$Q(F_{eq})$	−0.21	−0.48
	$Q(H_{ax})$	+0.25	+0.46		$Q(F_{ax})$	−0.19	−0.46
	$Q(O_{eq})$	−0.35	−0.83		$Q(H_{eq})$	+0.24	+0.51
	$Q(O_{ax})$	−0.32	−0.83		$Q(H_{ax})$	+0.32	+0.54
$CH_3^+(D_{3h})$	$-E$ (a.u.)	38.77948	39.17512				
	R(C–H)	1.08	1.12				
	Q(C)	+0.22	−0.03				
	Q(H)	+0.26	+0.34				
$F^-(H_2O)$	$-E$ (a.u.)	172.72635	175.21830	$F^-(HF)$	$-E$ (a.u.)	196.34485	199.21814
	R(O–H)	1.25	1.47		R(F–H)	1.18	1.26
	Q(F)	−0.68	−0.85		Q(F)	−0.67	−0.85
	Q(O)	−0.54	−0.92		Q(H)	+0.23	+0.54
	Q(H)	+0.22	+0.47		$Q(F(s))$	−0.46	−0.66
	Q(H′)	+0.01	+0.30				
$F^-(H_2O)_2$	$-E$ (a.u.)	247.77070	251.17407	$F^-(HF)_2$	$-E$ (a.u.)	295.00308	299.18257
	R(F–H)	1.28(1.23)	1.57		R(F–H)	1.26	1.38
	Q(F)	−0.55	−0.78		Q(F)	−0.55	−0.77
	Q(O)	−0.51	−0.91		Q(H)	+0.23	+0.54
	Q(H)	+0.24	+0.46		$Q(F(s))$	−0.46	−0.66
	Q(H′)	+0.04	+0.33				
$F^-(H_2O)_4$	$-E$ (a.u.)	397.9680	403.06199	$F^-(HF)_4$	E (a.u.)	492.25308	499.03659
	R(F–H)	1.40(1.26)	1.67		R(F–H)	1.38	1.57
	Q(F)	−0.43	−0.67		Q(F)	−0.42	−0.70
	Q(O)	−0.46	−0.90		Q(H)	+0.23	+0.52
	Q(H)	+0.23	+0.46		$Q(F(s))$	−0.37	−0.59
	Q(H′)	+0.09	+0.36				
$F^-(H_2O)_5$	$-E$ (a.u.)	472.75437	478.99080	$F^-(HF)_5$	$-E$ (a.u.)	590.84359	598.94370
	R(F–H_{eq})	1.46	1.80		R(F–H_{eq})	1.43	1.58
	R(H–F_{ax})	1.50	1.75		R(F–H_{ax})	1.48	1.68
	Q(F)	−0.39	−0.66		Q(F)	−0.42	−0.69
	$Q(O_{eq})$	−0.50	−0.89		$Q(H_{eq})$	+0.22	+0.51
	$Q(H_{eq})$	+0.25	+0.45		$Q(F_{eq})$	−0.32	−0.56
	$Q(H'_{eq})$	+0.10	+0.37		$Q(H_{ax})$	+0.22	+0.51
	$Q(O_{ax})$	−0.44	−0.89		$Q(F_{ax})$	−0.35	−0.56
	$Q(H_{ax})$	+0.22	+0.45				
	$Q(H'_{ax})$	+0.14	+0.37				
$F^-(H_2O)_6$	$-E$ (a.u.)	547.76190		$F^-(HF)_6$	$-E$ (a.u.)	689.43119	598.84526
	R(F–H)	1.52(1.30)			R(F–H)	1.49	1.72
	Q(F)	−0.43			Q(F)	−0.41	−0.68
	Q(O)	−0.42			Q(H)	+0.21	+0.50
	Q(H)	+0.21			$Q(F(s))$	−0.31	−0.55
	Q(H′)	+0.12					
F^{-b}	E (a.u.)	97.61331	99.24782				
H_2O^b	$-E$ (a.u.)	74.96590	75.90864	HF^b	$-E$ (a.u.)	98.57285	99.88729
	R(O–H)	0.99	0.96		R(F–H)	0.96	0.92
	H–Ô–H	100.0	111.2				
	Q(O)	−0.33	−0.80		Q(F)	−0.19	−0.48
	Q(H)	+0.16	+0.40		Q(H)	+0.19	+0.48

[a] Geometries are shown in Fig. 1; distances in Angstrom, angles in degree; s: solvent.

[b] Taken from Ref. [10]

[c] Values in parentheses refer to CNDO/2 optimized geometries.

quite different from a standard study of gas phase dissociation, where a configuration interaction calculation is surely needed in order to give a correct dissociative behaviour.

3. Results and Discussion

Molecules and Ions in Gas Phase. Total energies and geometries of the systems taken into consideration in the present work (H_2O, HF, CH_3^+, F^-), fully optimized by *ab initio* SCF MO calculations with STO-3G and 4-31G basis sets, were taken from Ref. [10]. The charges were calculated by us at the energy minima. $CH_3^+(s)_5$, s = HF, H_2O. The first solvation shell, in line with our previous semiempirical calculations [3] was simulated by five solvent units, set at the apices of a trigonal bipyramid, as shown in Fig. 1. Energies and optimized goemetries in the case of both solvents are collected in Table 1.

In hydrofluoric acid each HF solvent molecule points the fluorine atom towards the methyl carbon, as predicted by CNDO/2 method [3]. The axial (*ax*) and equatorial (*eq*) distances between the central carbon and the fluorine atoms are 1.81 and 1.71 Å at STO-3G level; 2.13 and 1.95 Å at 4-31G level, respectively. These values are larger than the corresponding ones predicted by the semiempirical method (CNDO/2: 1.66 and 1.52 Å, respectively). The positive charge on the solute (+1 in gas phase) is spread on the solvent molecules in solution, and reduces to +0.66 (STO-3G) and +0.81 (4-31G) in HF. This charge-transfer induced on the solvent seems to be overestimated by the minimal basis set calculation. Analogous behaviours occur in water, as shown by the data collected in Table 1.

$F^-(s)_n$, s = HF, H_2O, $n = 1$–6. The first solvation shell of fluorine anion in water and in hydrofluoric acid was investigated by considering different numbers of solvent units to describe it. Optimized solute–solvent distances (dotted lines) are shown in Fig. 1, and the optimized values of energy, geometry, and charges are collected in Table 1.

In this case also, *ab initio* solute–solvent distances appear systematically larger than those predicted by CNDO/2. Moreover, STO-3G distances are shorter than those obtained by *ab initio* calculations performed with optimized minimal basis sets also for F^- (e.g. in the case of $F^-(H_2O)$ [6]). The fact that CNDO/2 distances are shorter is not surprising bearing in mind that bond energies are generally overestimated by this computational technique.

The comparison of the present results with the previous ones obtained by CNDO/2 [2–4] shows that the two methods agree in predicting both the location and the orientation of the solvent units with respect to the solute. In general the agreement is better for clusters formed by a larger number of solvent units, where sterical hindrance (through-space interactions) prevails on through-bond interactions in defining the position of each solvent molecule. This fact was clearly shown in previous work on nitrogen–water interaction [12].

Table 2. *Ab initio* interaction energies[a] of $F^-(s)_n$ and $CH_3^+(s)_5$, $s = H_2O$, HF

System	$\mathscr{E}_{\text{int}}$[b] STO-3G	4-31G	E_{int}[b] STO-3G+BSSE[c]
$CH_3^+(H_2O)_5$	130.6	111.5	129.5
$CH_3^+(HF)_5$	100.1	76.3	100.0
$F^-(H_2O)$	92.3	38.8	29.9
$F^-(H_2O)_2$	132.2	68.4	37.0
$F^-(H_2O)_4$	200.7	112.1	43.7
$F^-(H_2O)_5$	210.9	153.3	45.8
$F^-(H_2O)_6$	221.6		45.3
$F^-(HF)$	99.6	52.1	36.6
$F^-(HF)_2$	153.8	100.5	49.0
$F^-(HF)_4$	218.6	150.4	61.0
$F^-(HF)_5$	229.7	162.8	60.4
$F^-(HF)_6$	238.9	171.7	57.7

[a] In kcal mol^{-1}

[b] for reference see [7, 8];

[c] calculated assuming $E[(s)_n] = n\mathscr{E}(s)$, see the text.

It appears from Table 1 that the negative charge of fluorine is spread on solvent molecules in solution, as expected. The extent of the charge-transfer is comparable in the two solvents. It increases with the number of the solvent units around the anion, and the effect predicted in minimal basis set calculations is surely overestimated, owing to the spurial central atom basis set extension in the solvated system.

In Table 2, the "interaction energy" of the solvated systems, calculated with STO-3G and 4-31G basis sets is reported ($\mathscr{E}_{\text{int}}$ in kcal mol^{-1}; for definition and reference see [6, 7, 13]). $\mathscr{E}_{\text{int}} = E[X(s)_n] - \mathscr{E}(X) - n\mathscr{E}(s)$, $\mathscr{E}(X)$ and $\mathscr{E}(s)$ being SCF energies (STO-3G; 4-31G) of the ion ($X = CH_3^+$, F^-) and of one solvent molecule ($s = H_2O$, HF), respectively. In the same table STO-3G interaction energies (E_{int}, kcal mol^{-1}) corrected for BSSE are reported in the fourth column. In our case $E_{\text{int}} = E[X(s)_n] - E(X) - E(S)$, where $E(X)$ and $E(S)$ are the STO-3G energies of the central ion and of the solvent cage S respectively, obtained using the same basis set as in the calculation of $E[X(s)_n]$. In solvated systems some problems arose for defining the geometry of the isolated solvent cage S, whose geometry is different from that of the cage including the ion. However we verified that $E(X)$ gives the main contribution to BSSE correction, owing to the position and the nature (in the case of F^-) of the ion X in the center of the solvated cage. In view of this E_{int} reported in Table 2 were calculated by assuming $E(S) = n\mathscr{E}(s)$.

It emerges from the data reported in the three columns of Table 2 that the absolute values of interaction energies calculated at different levels of approximation are quite different. It is known that after applying the counterpoise method a fairly large error still remains [6]. Moreover, for calculating interaction energies optimized basis sets should be used in order to give larger weight to the "tail" of the orbitals rather than to the region close to the origin [6,14]. These improvements are beyond the scope of the present treatment where we want to test the reliability of CNDO/2 in the description of geometries for the first solvation shell of organic molecules.

With reference to the experimental hydration energy (120 kcal mol^{-1} [15]) the 4-31G values seem to be the most realistic ones. However we note that this comparison is of dubious validity due to the different physical meaning of the above quantities.

$CH_3F(HF)_{11}$. In line with previous CNDO/2 calculations, eleven hydrofluoric acid units were used to describe the first solvation shell of fluoromethane in hydrofluoric acid. They correspond to the sum of six and five solvent units, used to describe the first solvation shell of the separated ions. These solvation numbers agree with the values indicated on the basis of thermodynamics and structural evidence [16].

As previously mentioned in Sect. 2, the dissociation energy profile of fluoromethane was calculated at several points of the C · · · F distance (r), keeping the solvent molecules at the positions previously optimized by CNDO [3]. Absolute and relative energies are reported in Table 3.

The dissociation curve in solution reported in Fig. 2 holds a qualitative significance only, since the calculated energies of the solvated fluoromethane at each r point are not really energy minima in this computational framework. The lack of geometry optimization justifies the discontinuous behaviour of the energy values as compared with the smooth curve obtained in the CNDO/2 calculation.

Table 3. *Ab initio* (STO-3G)[a] and CNDO/2[b] energies for the system $CH_3F(HF)_{11}$ computed at different C–F distances (in Å)

	STO-3G//CNDO		CNDO//CNDO	
C–F	$-E$ (a.u.)	ΔE (kcal mol^{-1})[c]	$-E$ (a.u.)	ΔE (kcal mol^{-1})
1.363	1221.698493	−316	349.9721	−101
1.5	0.152555	26.5	0.9387	−80
1.7	0.027730	104	0.8512	−26
2.0	1220.802528	392	0.7708	25
2.5	0.715372	479	0.7540	36
3.0	0.613702	364	0.7580	36
3.495	1221.284718	−56	0.9097	−62
4.0	0.138050	36	0.8243	−7
4.5	0.102789	58	0.8788	−43
5.0	0.210919	−10	0.9182	−68
5.665	0.303773	−68	0.9328	−77
6.0	0.256889	31	0.9163	−66
7.0	0.232400	24	0.8436	−21
10.0	0.194764	—	0.8105	—

[a] Geometries optimized by CNDO [5];
[b] see Ref. [3];
[c] $\Delta E = E[CH_3F(HF)_{11}] - E[CH_3F(HF)_5] - E[F^-(HF)_6]$ in kcal mol^{-1}.

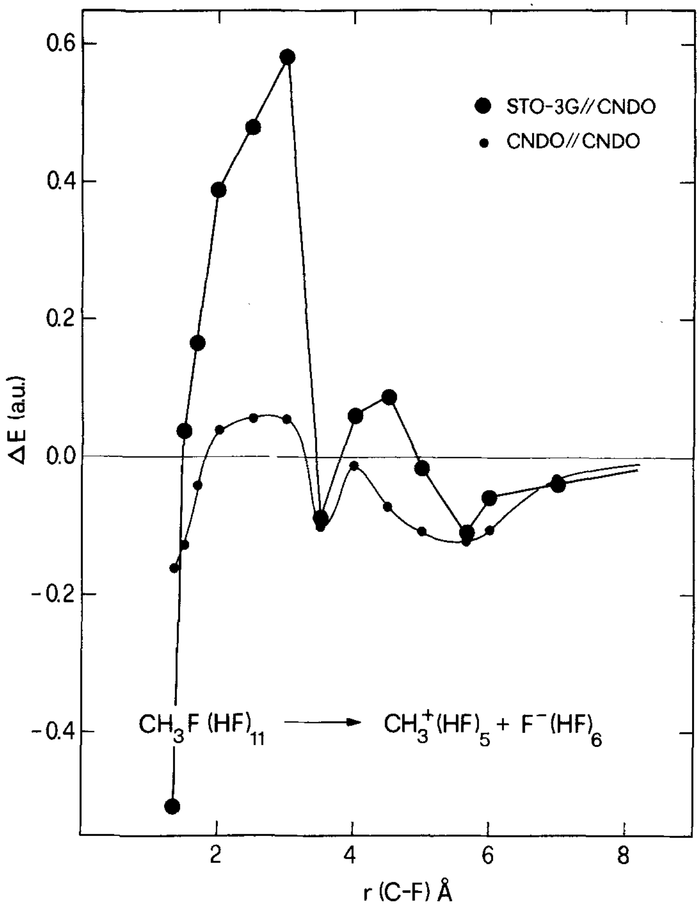

Fig. 2. *Ab initio* STO-3G//CNDO and CNDO energies ($\Delta E = E[CH_3F(HF)_{11}] - E[CH_3^+(HF)_5] - E[F^-(HF)_6]$) at several points of the dissociative path.

However we think that the presence in the *ab initio* dissociation curve of the same number of energy minima, at the same positions predicted by semiempirical calculations, is significant and strengthens the predictive ability of our solvent model, provided that it is employed in a full variable optimization process. It is gratifying that the same qualitative behaviour for alkyl halides, dissociating in a polar solvent, is predicted by three different model calculations, namely the *ab initio* MO-SCF method presented in this paper, the semiempirical CNDO/2 in our previous work [1–4], and the point-charge model recently exploited by Salem [17].

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