

Theoretical Investigation on the Role of Solvent in Solvolytic Reactions. Part 7.¹ The Enhancement of Solvolysis of Fluoromethane viewed by Voronoi Polyhedra

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The use of Voronoi polyhedra has been extended to the investigation of the solvolysis of CH₃F in different solvents.

In the last two decades considerable effort has been expended on developing suitable models to describe the nature of liquids and the way the structure of the bulk liquid is modified by the introduction of a solute, *i.e.* a neutral molecule or dissociated ion, acting as structure maker or breaker. Statistical methods such as Monte Carlo or molecular dynamics and static models have been applied and particular attention was devoted to the first solvation shell and its influence both on the solute conformation and on the mechanism of chemical reactions.

With a framework of static models we have studied¹⁻⁶ the effect of the solvent on different observables, such as electronic spectra, conformations, and dissociation energies of solvated molecules, and the results were always reliable and consistent with experiment. According to our model the solvent effect is described by a limited number of solvent units which are bound to the solute for times sufficiently long that they participate in its diffusive motion.

More recently, Voronoi polyhedra,^{7,8} have been assumed to give a coherent description of the solvent cage of complex solutes in water solution.⁹ In a preliminary investigation¹⁰ we introduced Voronoi polyhedra as an aid to understanding the local solvent structure of simple systems, models for reagents and products of halogenoalkyl solvolytic reactions, previously investigated by semiempirical quantum mechanical methods including the solvent effect.^{1,3-6} Voronoi polyhedra give a clear view of the extent of solvation both of a complex solute and of part of it, so that they can be used successfully to define the minimum number of solvent units to be taken into account for a proper description of the first solvation shell of molecules and ions.

In this paper we consider the simple solvolytic reaction of fluoromethane in water and other solvents. Our aim is to follow the enhancement of solvolysis through the variation of the shape and the volume of the Voronoi polyhedra centred on the carbon and fluorine atoms of CH₃F at several values of the dissociation co-ordinate C-F. Moreover, the effect of different solvents, such as hydrofluoric acid and methane, is considered in terms of the variation of shape and extension of the corresponding polyhedra. The data necessary to build up Voronoi polyhedra, *i.e.* the co-ordinates of the solvent units forming the first solvation shell, are available from previous work, where the dissociation reaction of CH₃F in H₂O,⁴ HF,¹¹ and CH₄¹² was investigated.

The definition of the polyhedra is given in the Appendix, where the details of their construction, previously discussed in the literature (see for example ref. 13), is exemplified taking nitromethane as a simple model for a solvated organic molecule.

The polyhedra centred on C and F atoms of CH₃F are constructed by taking into account all the atoms of the solvent

molecules in the case of H₂O and HF, while in the case of CH₄ the calculations were performed both including and excluding hydrogen atoms.

Results

In a previous paper¹⁰ CH₃F and its dissociation products were studied in water only. The Voronoi polyhedron for an atom of a solute molecule would be, to a large extent, independent of the model employed for the solvent when a large number of solvent units is considered. However, the shape of the polyhedron is specifically defined when a reduced number of solvent units is used to build up the first solvation shell. The six water molecules generally used for the first solvation shell of fluorine anion generate a cubic structure for the corresponding polyhedron, and the five water molecules solvating the methyl cation give rise to a prism with triangular base. The shape of the polyhedron, which depends on the number of solvent units, is almost independent of the solvent. Unlike the shape, the volume depends on the solute-solvent distance, *i.e.* on the strength of solute-solvent interaction. For F⁻ the volume of a Voronoi cubic polyhedron is 2.55 Å³ in HF, 2.75 Å³ in H₂O, and 3.70 Å³ in CH₄. The volumes of Voronoi polyhedra for CH₃⁺, calculated considering all solvent atoms, correspond to 2.51, 2.49, and 2.40 Å³ for HF, H₂O, and CH₄, respectively. It appears that the polyhedron volume is inversely dependent on the solvation strength. The volume increases when the solvent hydrogens are not considered. Another parameter characterizing the solvation contribution for a specific solvent molecule is the extension of the faces of the polyhedron. The area of the faces is related to the interaction between the solute and a specific solvent atom. Small variations of the area of the faces during the reaction enhancement are associated with a limited motion of the corresponding solvent molecule. Large and sudden variations of the areas of some faces reveal large displacements of the associated solvent molecules in the space around the solute, during the course of the reaction.

The most relevant data related to the solvolysis of CH₃F in H₂O, HF, and CH₄ are shown in Tables 1-3, where the volumes of the polyhedra centred on C and F atoms and the areas of the most important sets of faces are listed for several values of C-F distance. The data provide quantitative information on the effect of each considered solvent. A pictorial view of the enhancement of the solvolysis of CH₃F in terms of Voronoi polyhedra is shown in Figures 1-3, for a limited number of values of the dissociation co-ordinate. Volumes and areas in the three Figures are given on a common scale, and the solvent molecules generating the polyhedra faces are also reported.

Table 1. Volumes (\AA^3) and face areas (\AA^2) of the Voronoi polyhedra centred on the C and F atoms for the dissociation reaction of CH_3F in H_2O

C-F	Volume		C polyhedron face area ^a					F polyhedron face area ^a				
	C	F	L ^b	3,4,5 ^c	6	9	24	3,4,5 ^c	22	25	28,31 ^c	34,37 ^c
1.388	2.56	4.20	2.47	3.05	0.00	0.83		0.82	0.96		2.33	2.39
2.5	2.80	5.19	0.42	3.41	0.00	2.72		1.66	0.36	0.09	2.79	3.09
3.48	3.65	3.03		2.84	1.23	0.09	2.84		2.07	2.34	2.08	2.07
4.0	3.27	3.06		3.44	2.65	0.37	1.60		1.86	2.47	2.12	2.05
5.463	2.67	2.96		3.19	2.67	0.83			1.98	2.48	2.04	2.00
∞	2.49	2.75		2.96	1.62	1.62			1.96	1.96	1.96	1.96

^a The faces are identified by the numbering of the generating atoms, see Figure 1. ^b Face common to the C and F polyhedra. ^c Mean of the areas generated by atoms in the heading.

Table 2. Volumes (\AA^3) and face areas (\AA^2) of the Voronoi polyhedra centred on the C and F atoms for the dissociation reaction of CH_3F in HF

C-F	Volume		C polyhedron face area ^a					F polyhedron face area ^a				
	C	F	L ^b	3,4,5 ^c	6	7	20	6	8	10	12,14 ^c	16,18
1.363	2.72	5.16	2.81	3.13	0.14		0.41	2.20	2.41	3.04	1.36	1.40
1.5	2.77	5.34	2.57	3.17	0.10		0.79	2.27	2.51	3.00	1.36	1.40
2.0	2.77	5.47	1.12	3.30	0.07		2.09	3.00	3.18	3.38	1.12	1.23
3.0	2.77	5.88		3.12	0.21	0.60	3.37	5.34	3.55	4.72	2.22	1.45
3.495	2.66	6.60		3.18	2.80		0.72		2.68	4.66	3.05	1.18
4.0	2.57	5.50		3.04	1.47		1.86		2.59	4.15	3.03	1.21
4.5	2.53	2.99		2.99	1.85		1.50		2.05	2.07	2.47	1.53
5.0	3.00	3.55		3.48	1.80	0.28	1.50		2.54	2.05	2.65	1.54
5.665	2.69	2.51		3.17	2.27	0.02	1.21		1.90	1.88	1.93	1.73
7.0	2.89	2.58		3.38	1.86	0.12	1.55		1.88	1.88	1.91	1.86
10.0	2.84	2.56		3.33	1.85	0.11	1.57		1.88	1.88	1.87	1.87
∞	2.51	2.55		2.97	1.66		1.66		1.87	1.87	1.87	1.87

^a The faces are identified by the numbering of the generating atoms, see Figure 2. ^b Face common to the C and F polyhedra. ^c Mean of the areas generated by atoms in the heading.

Table 3. Volumes (\AA^3) and face areas (\AA^2) of the Voronoi polyhedra centred on the C and F atoms for the dissociation reaction of CH_3F in CH_4

C-F	Volume		C polyhedron face area ^a				F polyhedron face area ^a					
	C	F	L ^b	3,4,5 ^c	7	21,22 ^c	3,4,5 ^c	17,18 ^c	35	39	43	47
1.345	2.67	10.33	2.83	3.12		0.01	1.17		8.39	5.30	5.27	5.33
2.0	2.47	5.37	0.47	2.68	0.31	1.48	1.35		2.96	3.81	3.77	3.65
2.5	2.39	5.19		2.56	0.46	1.72	0.58		4.54	4.50	4.53	4.44
3.0	2.39	5.80	0.02	2.58	0.43	1.71	0.04		7.03	5.39	5.46	5.43
3.5	2.38	9.99		2.54	0.48	1.73	3.15		1.05	6.50	6.34	6.35
4.0	2.36	6.94		2.52	0.45	1.70		0.52	9.39	4.73	5.86	5.98
4.5	2.38	7.36		2.56	0.47	1.71		0.94	9.80	3.88	5.90	6.24
5.0	2.38	7.90		2.56	0.47	1.70		0.26	11.03	5.03	8.43	5.60
5.5	2.39	6.90		2.60	0.45	1.68		0.66	9.29	4.13	5.99	6.00
6.0	2.48	5.62		2.70	0.41	1.66			6.81	5.10	5.33	5.38
7.0	2.36	5.70		2.56	0.45	1.69			7.11	5.38	5.40	5.47
∞ ^d	2.40	5.44		2.41		0.99 ^e			5.55	5.55	5.55	5.55

^a The faces are identified by the numbering of the generating atoms, see Figure 3. ^b Face common to the C and F polyhedra. ^c Mean of the areas generated by the heading atoms. ^d Polyhedra related to $\text{CH}_3^+(\text{CH}_4)_5$ and $\text{F}^-(\text{CH}_4)_4$ solvated ions. ^e Hydrogens 17 and 18 generate faces with areas 0.99\AA^2 .

CH_3F in Water.—The dissociation curve of CH_3F in H_2O , previously obtained by semiempirical calculations,⁸ shows three minima, related to the structure of the dissolved but undissociated CH_3F and two different kinds of ion pairs. The Voronoi polyhedra reported in Figure 1 refer to the three minima at C-F 1.39, 3.48, and 5.46 \AA , and two maximum points at 2.5 and 4.0 \AA . The numerical data are collected in Table 1 where only faces with areas larger than 1\AA^2 are reported. It appears that the separation of the two ions becomes evident at C-F 2.5 \AA , where the extension of the face common to the two polyhedra centred on C and F (darkened in the Figure) reduces to 0.42\AA^2 .

Starting from C-F 3.48 \AA the presence of solvent-separated ion pairs is clearly evidenced by the polyhedra. The link between the two polyhedra is assured by two water molecules (labelled 6 and 24,25 in Figure 1), but only one (24,25) generates faces on both polyhedra. The other water molecule (6), even if it is located in the region between the two ions, belongs to the hydration shell of CH_3^+ only. The picture evolves regularly on increasing C-F and shows the expected separation of $\text{CH}_3^+(\text{H}_2\text{O})_5$ and $\text{F}^-(\text{H}_2\text{O})_6$. At C-F 5.46 \AA the Voronoi polyhedra emphasize the structure of a solvent-separated ion pair, in which the link between the two solvated counterions is provided by the hydrogen bond formed by water molecules 6 and 24,25.

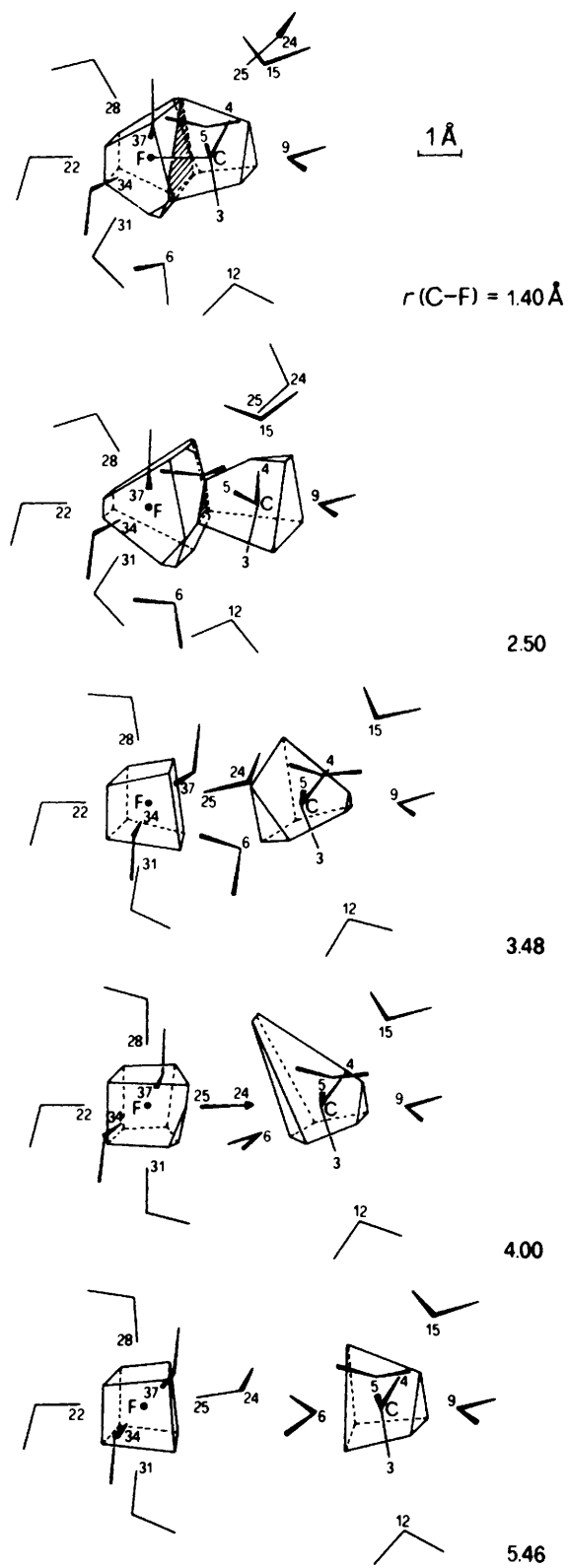


Figure 1. Dissociation of CH_3F in H_2O versus C-F viewed by the Voronoi polyhedra centred on the C and F atoms. The solvent molecules generating the polyhedra are also depicted; the numbering is limited to the atoms which generate polyhedra faces. Darkened areas represent the faces connecting the two polyhedra

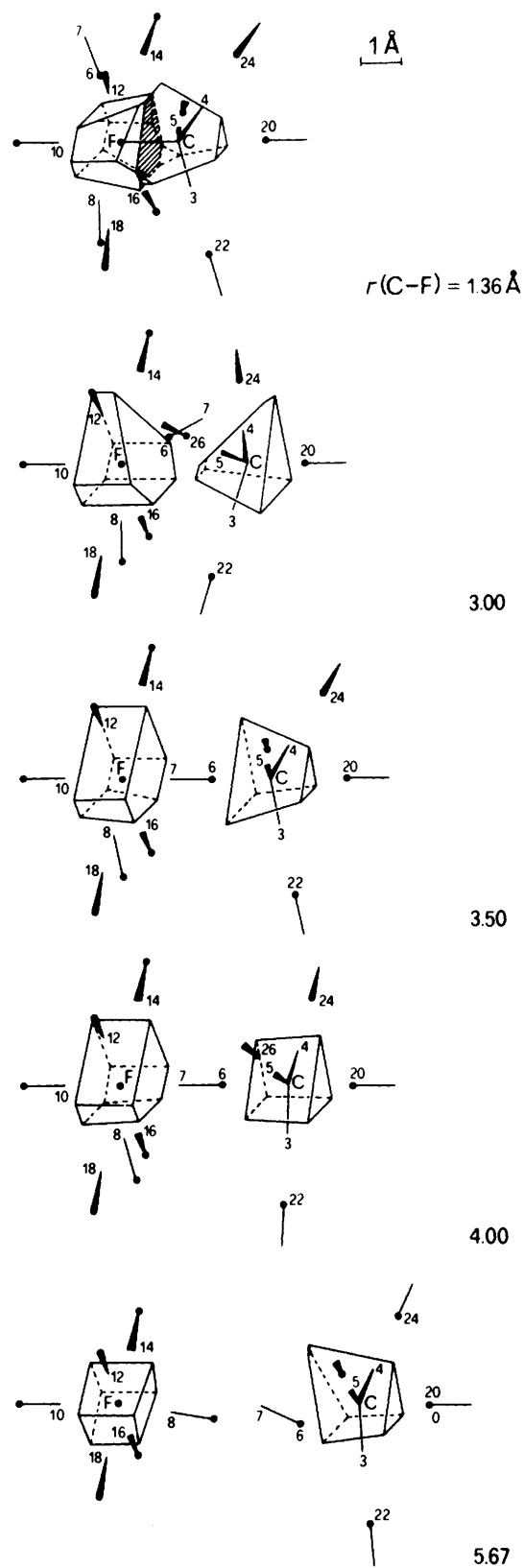


Figure 2. Dissociation of CH_3F in HF versus C-F viewed by the Voronoi polyhedra centred on the C and F atoms. The solvent molecules generating the polyhedra are also depicted; the numbering is limited to the atoms which generate polyhedra faces. Darkened areas represent the faces connecting the two polyhedra

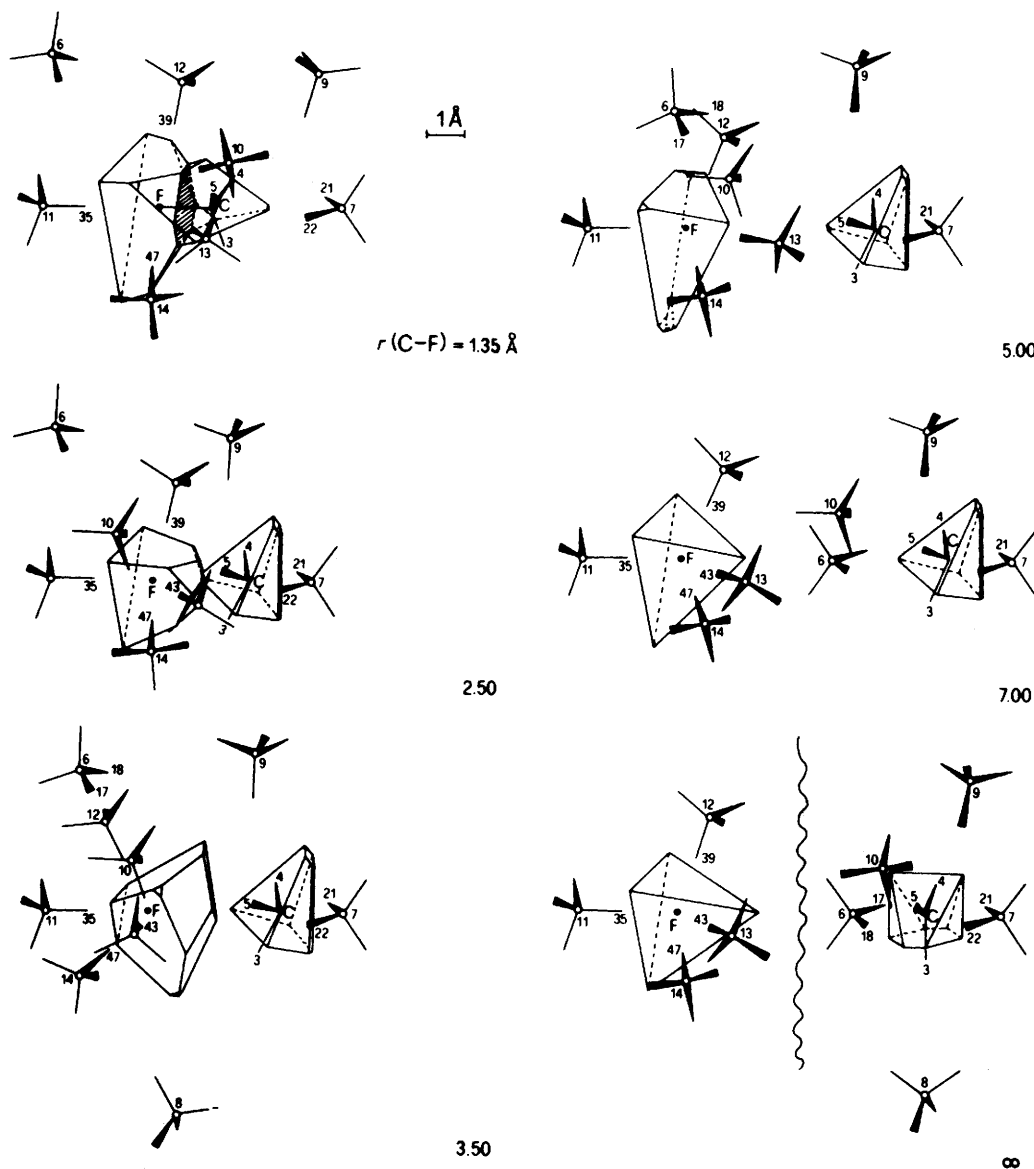


Figure 3. Dissociation of CH_3F in CH_4 versus C-F viewed by the Voronoi polyhedra centred on the C and F atoms. The solvent molecules generating the polyhedra are also depicted; the numbering is limited to the atoms which generate polyhedra faces. Darkened areas represent the faces connecting the two polyhedra

The behaviour of the other water molecules at different values of the C-F distance can be explained by the variation of the extensions of the corresponding faces. Obviously, faces of the polyhedron centred on C, generated by methyl hydrogens, remain practically independent of C-F , as the water molecules co-ordinated to these hydrogens cannot give any contribution to the formation of the C polyhedron, because they are cut off by methyl hydrogens. Water molecule 9 always remains co-ordinated to methyl C and stays on the opposite side with respect to the F atoms. The variations of its face extension is due more to slight changes of HCH angles than to significant displacements of the molecule itself. Likewise variations of the areas of the faces generated by water molecules labelled 22, 28, 31, 34, and 37 in Figure 1 are small owing to persistent co-ordination to the F atom. The only exception is the area of the face generated by water molecule 22, whose variation with C-F is mainly due to slight concerted displacements of the other solvent molecules in the locality.

The changes in shape of the polyhedra versus C-F show the right dissociative behaviour and indicate the formation of solvated ions. The number of water molecules (11) taken into account to solvate CH_3F , even if small, is sufficient to describe both the first solvation shell and to predict correctly solvation effects during solvolysis of this molecule in water.

CH_3F in HF.—The dissociation curve of CH_3F in HF¹¹ is very similar to that predicted for H_2O , and this finding is reasonable by considering that both solvents are highly polar [$\epsilon(\text{H}_2\text{O})$ 80, $\epsilon(\text{HF})$ 84] and are structured by strong hydrogen bonds. Inspection of Figures 1 and 2 shows similar qualitative pictures in terms of Voronoi polyhedra. Volumes and areas of the faces reported in Tables 1 and 2 strengthen this similarity quantitatively.

The structures of two ion pairs separated by one and two HF molecules, labelled 8 and 6,7 respectively, are evident in Figure 2. Both solvent units come from the solvation shell of fluorine,

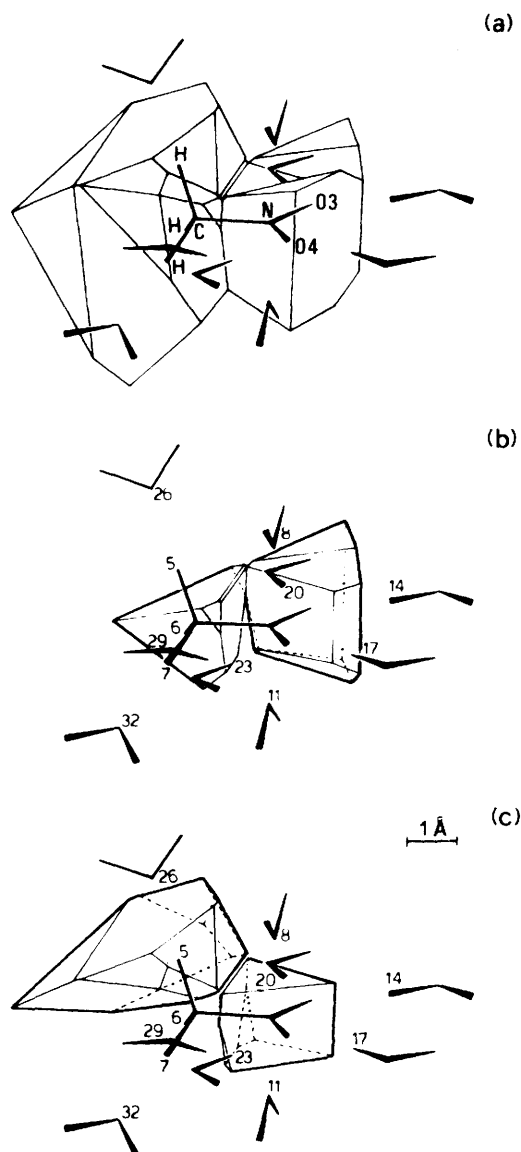


Figure 4. Voronoi polyhedra for nitromethane: (a) the whole polyhedron; (b) C and N atom polyhedra; (c) N and H atom polyhedra. The H_2O molecules generating the polyhedra are also depicted; the numbering of the atoms of solvent molecules is limited to the atoms generating polyhedra faces. Optimized CNDO/2 parameters for $\text{CH}_3\text{NO}_2(\text{H}_2\text{O})_6$ system: $E(\text{a.u.}) = -57.9421$; $r(\text{C}-\text{N}) = 1.417$ (1.46) Å; $r(\text{N}-\text{O}) = 1.244$ (1.21) Å; $r(\text{C}-\text{H}) = 1.117$ Å; $\angle \text{CNO} = 119.1$ (116.5); $\text{HCN} = 110.1$; $q(\text{C}) = -0.02$ e; $q(\text{N}) = +0.50$; $q(\text{O}) = -0.03$; $q(\text{H}) = +0.06$ (averaged value). Gas-phase electron diffraction data reported in parentheses.¹⁵ X-Ray data at low temperatures are available in refs. 16 and 17

but their insertion between the two ions occurs in successive stages of the dissociation process. The other HF molecules show the same behaviour described for H_2O solvent molecules.

The volume of the polyhedron centred on C atom is independent of C-F, unlike that centred on F atom. The latter volume reduces drastically to half its value at C-F distances 4 Å, owing to the presence of one extra HF molecule around the F atom at the lowest C-F distances. As C-F increases, CH_3^+ carries this HF unit (6,7) so that another HF molecule (8,9) is allowed to get in the right position for better solvation of the fluorine anion.

CH_3F in CH_4 .—The trend of the dissociation curve of CH_3F in CH_4 ¹² does not show local minima. The solvolysis in CH_4 is quantitatively described by the data reported in Table 3 and illustrated by the polyhedra centred on C and F atoms, collected in Figure 3 at several values of the C-F distance. Solvent hydrogens were included to build up the polyhedra.

First, it appears that Voronoi polyhedra on the C atom have volumes comparable with those in the other solvents, while the F polyhedra are significantly larger than those generated in H_2O and HF. As a consequence the ratio between the volumes of F and C centred polyhedra is higher than the corresponding value for the other solvents. This fact is due to the reduced number of solvent units, namely nine, used to describe the first solvation shell in CH_4 , causing an insufficient degree of solvation on F.

The disappearance of the face common to the two polyhedra defines the point where the dissolved CH_3F separates in solvated ions. Unlike in H_2O and HF, we observe in CH_4 strong variations of the areas of a few faces of the polyhedra. Faces generated by 35, 39, 43, and 47 atoms on the F polyhedron are significant examples. Moreover, the solvent molecule 6, originally placed far from the solute on the side of the F atom, approaches this atom as C-F increases, up to C-F 5.5 Å. Then, it enters the region between the two ions. The higher mobility of the CH_4 solvent units, well described by the corresponding large variation of the areas of the polyhedra, are easily explained by the low polarity of the solvent and the absence of hydrogen bonds. Voronoi polyhedra shown in Figure 3 suggest that the number of CH_4 molecules used is inadequate for a good description of the first solvation shell. In fact, at the highest C-F distances F^- and CH_3^+ are solvated by five and four CH_4 molecules, respectively. However, at large C-F distances the CH_4 molecule 6 show, a weak interaction both with F^- and CH_3^+ . To test how shapes and volumes of polyhedra depend on methane hydrogen orientation we have calculated Voronoi polyhedra disregarding the presence of CH_4 hydrogens. Volumes and areas greatly increase, in particular in F-centred polyhedra, but the solvent units generating faces are the same in both calculations. At least two solvent units have to be added to assure realistic solvation for CH_3F in CH_4 .

Conclusions.—The use of Voronoi polyhedra to display the extent and the role of solvation on the course of dissociation reactions is the goal of the present investigation. We are well conscious of the level of approximation of the semiempirical quantum mechanical calculations employed to describe the solvolysis of CH_3F and the very low number of solvent units considered to represent the static model of the first solvation shell. This rough model was however used with the aim of showing how Voronoi polyhedra can offer information on the effect of the solvent at each stage of the course of a chemical reaction. Obviously, this procedure can be applied when a very large number of solvent units is introduced in the model and its energetics is obtained by means of *ab initio* calculations. The pictures collected in Figures 1–3 represent a static view of one among infinite configurations existing during the dynamical evolution of the solvent, which can be followed either under molecular dynamics or Monte Carlo conditions.

On the whole, Voronoi polyhedra can provide the following type of information. (a) An insufficient model of solvation of a solute is unequivocally revealed when closed polyhedra around the solute cannot be constructed. (b) During the course of the reaction they give a view of the extent of solvation of each dissociating species and define easily the domain of existence of the different kinds of species in solution, such as solvated but undissociated molecules, different types of ion pairs, and solvated free ions. (c) On quantitative grounds the relative comparison of the polyhedra volumes generated by different

solvents is a measure of the solvating power of each solvent. A volume drop emphasizes a better structuration of the solvent. The variation of the areas generated by a specific solvent unit during the reaction course allows its displacement to be followed during the reaction enhancement. (d) Lastly, Voronoi polyhedra are a useful tool to define the limits of the displacements of each solvent molecule both in the domain of its solvation shell, and between different shells of solvation along the reaction path of a chemical reaction.

Appendix

Voronoi Polyhedra Construction.—To build up the polyhedra centred on a given atom A, one considers another atom J and the plane H(J), perpendicular to the segment A–J, and intersecting it at its middle point. The H(J) plane subdivides the space in two parts, one of which, defined $H^+(J)$, contains the atom A. The intersections of the $H^+(J)$ semispaces generated by all solvents and solute atoms (different from A) set up the Voronoi polyhedron. In other words, given a set of atoms A_i , $1 < i < n$, the Voronoi polyhedron V_i around atom i is the set of points closer to A_i than to any A_j ($j \neq i$). The details of the geometrical properties of these polyhedra have been given previously.¹³

To illustrate the construction and the analysis of the Voronoi polyhedra of an organic molecule in solution we chose a small cluster of nitromethane in water, namely the system $\text{CH}_3\text{NO}_2 \cdot (\text{H}_2\text{O})_9$. The geometry of the cluster was obtained by an energy-minimization procedure using the CNDO/2 approximation.¹⁴ The relevant energy and geometry parameters optimized for the $\text{CH}_3\text{NO}_2 \cdot (\text{H}_2\text{O})_9$ system are reported in the caption of Figure 4. In Figure 4 the whole polyhedron (a), and the polyhedra centred on C and O atoms (b), and N and H atoms (c) are shown. The water molecules generating the polyhedra are also shown. In detail, the solvent molecules labelled 8 and 11 in Figure 4 solvate the N atom [$\text{N} \cdots \text{O}(8)$ 1.518 Å; $\widehat{\text{CNO}}(8)$ 92°]. The two oxygens of CH_3NO_2 are solvated by the water molecules 14, 17, 20, 23 [$\text{O} \cdots \text{O}(14) = \text{O} \cdots \text{O}(17)$ 1.475 Å; $\widehat{\text{NOO}}(17)$ 177.8°; $\widehat{\text{NOO}}(14)$ 220.5°] and the three remaining H_2O molecules are located near the three hydrogens of CH_3NO_2 [$\text{H} \cdots \text{O}(26)$ 1.619 Å].

The volumes (in Å³) of the polyhedra centred on the atoms of CH_3NO_2 were obtained by the calculation: $V(\text{C})$ 2.83; $V(\text{N})$ 3.24; $V(\text{O})$ 5.57; $V(\text{H})$ 12.07 (averaged value), as well as the area (in Å²) of the polyhedra common to each pair of atoms: $A(\text{C},\text{N})$ 2.89; $A(\text{C},\text{H})$ 3.29; $A(\text{N},\text{O})$ 3.25; $A(\text{O},\text{O})$ 0.84; $A(\text{H},\text{H})$ 6.39 (averaged value).

The inspection of both Figure 4 and of volumes and areas of the polyhedra allows the following points to be made. (a) The C atom polyhedron is due to the molecular bonds generating the

four dominating faces. (b) In the same way, the three molecular bonds and the two H_2O molecules 8 and 11 generate essentially the N atom polyhedron. (c) Conversely, the O atom polyhedrons are mainly due to N atom and solvent molecules 14, 20, 8, and 11, and at a lesser extent to the other oxygen. (d) The polyhedra associated with each nitromethane hydrogen are mainly due to the water molecules directly co-ordinated to it, to the C atom, and the other two hydrogens; the other solvent units, namely 8, 11, 20, and 23, give a much smaller contribution. Lastly, it appears in the case of this rough model of solvation, that the nitro group co-ordinates a number of solvent molecules larger than methyl group does, namely six out of nine. The volume of the whole polyhedron, which is a measure of the co-volume of CH_3NO_2 as measured by water solvent, is 53.42 Å³, which corresponds to an equivalent radius of ca. 2.34 Å.

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