Geometry and Electronic Structure of Intimate and Solvent-separated Ion Pairs of Fluoromethane in Water

By **Pietro Cremaschi, Aldo Gamba,** and **Massimo Simonetta,*** C.N.R. Centre and Physical Chemistry Institute of the University, Via C. Golgi 19, I-20133 Milan, Italy

A semiempirical calculation on fluoromethane in water has been perfomed to establish the number and kind of different ion pairs, whose existence has been suggested as intermediates in solvolytic reactions. The calculations predict the existence of three species; their geometric and electronic structures are discussed.

THE relevance of ion pairs in solvolysis and exchange reactions has long been stressed,[1] but the role of ion pairs and/or carbonium ions in solvolysis is still a controversial subject and evidence for the intervention of ion pairs during solvolysis reaction has been recently reviewed.[2]

After differentiation between dissociated carbonium ions and carbonium ion pairs, two kinds of ion pair were recognized in Winstein's work,[1] namely an intimate ion pair, which consists of two ions in contact, in the same solvent cage, and a solvent-separated ion pair, more reactive to salts and nucleophilic agents, described as a pair of ions in separate, but adjacent solvent cages.

The scope of Winstein's theory has been extended in two respects: (*a*) primary and methyl substrates have been shown to react according to the ion pair mechanism;[3] (*b*) besides solvolysis and exchange, elimination reactions have been discussed in terms of a unified ion pair mechanism.[4]

According to these premises, Scheme 1 can be formulated for a solvolytic reaction. The initial substrate and each of its ionic modifications can react with a solvent molecule to give the product; the assumption is usually made that k_{1s} is kinetically insignificant.[4]

Scheme 1 is derived from a well established experimental basis. However no information has ever been produced on the structure of the two kinds of ion pair, neither theoretically nor experimentally. All descriptions given up to now are presented in very vague form.

In the present work we study, through the application of MO theory, a simple case, fluoromethane in water. The choice of this system is based on two facts: it has

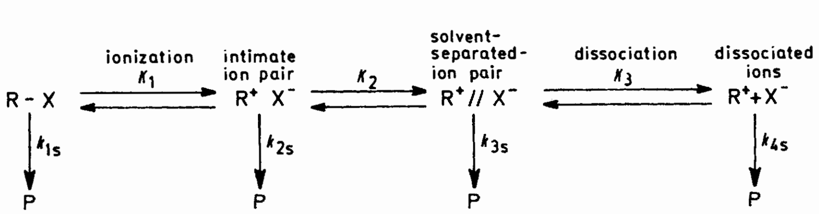
---

[1] S. Winstein, in ' Chimica Teorica,' Acc. Naz. Lincei, Roma, 1965, p. 307.

[2] D. J. Ruber, J. Milton Harris, and P. v. R. Schleyer, in ' Ions and Ion Pairs in Organic Reactions,' ed. M. Szwarc, Wiley-Interscience, 1974, vol. 2.

[3] J. M. W. Scott, *Canad. J. Chem.*, 1970, **48**, 3807.

[4] R. A. Sneen, *Accounts Chem. Res.*, 1973, **6**, 46.



SCHEME 1

been thoroughly studied by means of kinetics[3] and thermodynamics,[5] and it is perhaps the one in which the smallest possible molecular dimensions are involved. In particular the dimensions of the alkyl halide allow a solvent cage to be built with a small number of solvent molecules. In fact we can describe our system as formed by one CH_3F and 11 H_2O molecules.

The energy and electronic charge distribution in this supermolecule have been calculated for different geometries by means of the standard CNDO/2 method.[6] This particular technique was chosen since it proved to lead to satisfactory results for a number of problems in which the influence of the solvent (water) on chemical and spectroscopic phenomena was under study.[7-10] As a further test of the reliability of CNDO/2 results when dealing with solvation problems, we also performed calculations for the solvation energy of the ammonium ion, for which accurate experimental data are available.[11]

CALCULATIONS

The calculations were performed by using the CNDO/2 method with standard parametrization.[6] The program used includes an energy minimizing process which iteratively optimizes the geometrical parameters through a quadratic interpolation, until a self-consistent set of values is obtained. In the case of the largest systems, where not all parameters have been optimized, the calculated minima have been confirmed by repeating the iterative process with different starting geometries.

All geometrical parameters have been optimized for H_2O, NH_3, NH_4^+, CH_3F, and CH_3^+. In the case of the solvated systems $(F,6H_2O)$, $(CH_3,5H_2O)^+$, $(CH_3F,11H_2O)$, $(NH_4,nH_2O)^+$, and $(NH_4,nNH_3)^+$ (n = 1—5), a limited number of geometrical variables was considered; the geometry of the solvent units was kept rigid and local symmetry of the solute retained.

The $(CH_3F,11H_2O)$ system has been studied for different C-F distances, keeping the fluorine atom along the C_3 axis of the methyl group.

RESULTS

The minimum energy geometries and charge distributions for H_2O and CH_3F have been previously calculated by us and are available in ref. 7.

(1) NH_3, NH_4^+, $(NH_4,nH_2O)^+$, *and* $(NH_4,nNH_3)^+$ (n = 1—5).—The minimum energy geometry for NH_3 corresponds to a bond length of 1.067 Å and a bond angle of 113° 42′. The corresponding energy is $-13.889\,8$ a.u. For tetrahedral NH_4^+ the optimized value of the N–H bond is 1.077 Å, corresponding to $E_{tot} = -14.367\,6$ a.u.

In the case of solvated systems the geometry of the solvent units and of the ion was kept fixed, while the solute–solvent distance was optimized. The minimum energy approach was found along the N–H bonds. In the case of the penta-solvated supermolecule the first four solvent units were assumed fixed at the equilibrium distance of the tetra-solvated molecule; the fifth was added externally along an N–H or O–H bond of a solvent molecule of the first solvation shell.

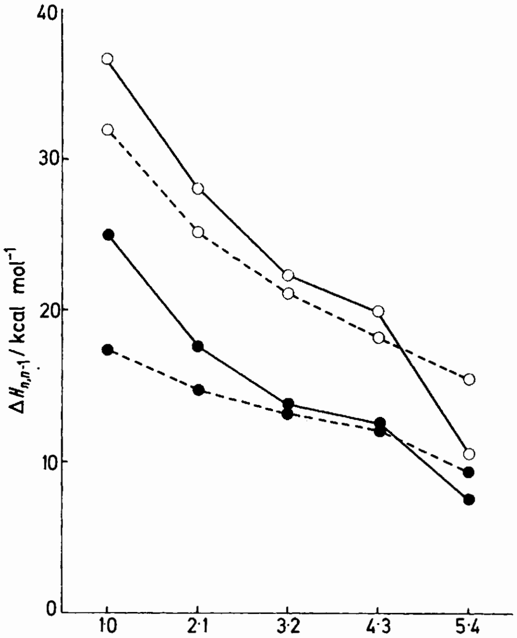


FIGURE 1 Calculated (○) and experimental (●) values of $\Delta H_{n,n-1}$ (n = 1–5) for successive addition of ligands to NH_4^+ Full lines for $(NH_4,nNH_3)^+$; dotted lines for $(NH_4,nH_2O)^+$

The calculated values of $\Delta H_{n,n-1}$ for successive addition of ligands (NH_3 or H_2O) to NH_4^+ are shown in Figure 1, together with the experimental curves.[11] The qualitative features of the experimental data are well reproduced, in line with recently published *ab initio* calculations.[12]

(2) CH_3^+.—A planar conformation with C_3 axis and

---

[5] D. N. Glew and E. A. Moelwyn-Hughes, *Discuss. Faraday Soc.*, 1953, **15**, 150.

[6] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.

[7] P. Cremaschi, A. Gamba, and M. Simonetta, *Theor. Chim. Acta*, 1972, **25**, 237.

[8] P. Cremaschi, A. Gamba, and M. Simonetta, *Theor. Chim. Acta*, 1973, **31**, 155.

[9] P. Cremaschi and M. Simonetta, *Theor. Chim. Acta*, 1975, **37**, 341.

[10] P. Cremaschi and M. Simonetta, *J. Mol. Structure*, 1975, **29**, 39.

[11] J. D. Payzant, A. J. Cunningham, and P. Kebarle, *Canad. J. Chem.*, 1973, **51**, 3242.

[12] A. Pullman and A. Armbruster, *Chem. Phys. Letters*, 1975, **36**, 558.

bond length 1.118 Å is associated with the minimum energy E_{tot} −8.671 8 a.u. This geometry is in substantial agreement with results of *ab initio* calculations which predict a bond length of 1.120 (STO-3G) or 1.076 Å (4—31 G) with a $\widehat{HCH}$ angle of 120°.[13]

(3) $(F,6H_2O)^-$.—The choice of a symmetric octahedral cage has been previously discussed by us[7] and more recently substantiated by sophisticated calculations by Clementi and others.[14] Within the approximation of rigid water molecules and the assumed octahedral symmetry, the F···H distance corresponding to the minimum energy (E_{tot} −147.126 5 a.u.) is 1.401 Å (see Figure 2a).

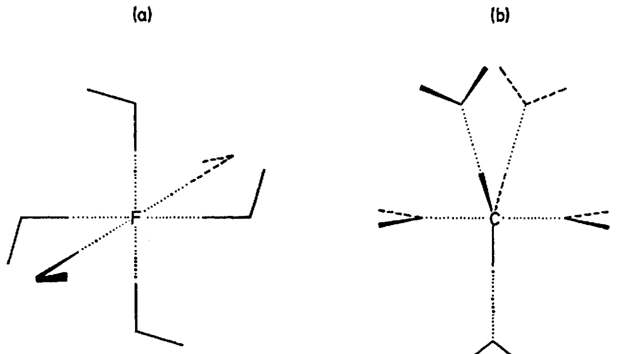


FIGURE 2 Molecular packing: (a) $(F,6H_2O)^-$; (b) $(CH_3,5H_2O)^+$

(4) $(CH_3,5H_2O)^+$.—For the solvent cage around a planar CH_3^+ ion, a bipyramidal trigonal symmetry was assumed, with water oxygens pointing towards the central cation. The C–H bond length has been kept constant at 1.118 Å. Through the optimization of the two variables r(C···O) and r(H···O), the following values were obtained at the energy minimum: E_{tot} −108.636 4 a.u., r(C···O) 1.529 Å, r(H···O) 1.647 Å. Free rotation of the water molecules around their symmetry axis has been verified. The final geometry is shown in Figure 2b.

Geometric parameters and total energies for $(CH_3F,11H_2O)$, evaluated at different C–F distances

r(C–F) (Å)	1.388	2.500	3.480	4.000	5.463
Variable					
Distance (Å)					
1–6	2.695	2.999	1.705	1.426	1.439
2–25	2.997	3.223	1.224	1.248	1.203
3–12; 4–15; 5–18	1.819	1.618	1.770	1.696	1.717
1–9	1.799	1.411	2.253	1.958	1.784
2–28; 2–31	1.613	1.410	1.486	1.439	1.464
2–34; 2–37	1.587	1.337	1.457	1.476	1.480
2–22	1.797	1.958	1.491	1.471	1.465
Angle (°)					
6–1–39	44.7	55.7	64.9	72.0	88.7
25–2–22	223.5	220.9	194.8	205.9	198.8
3–1–2; 4–1–2; 5–1–2	100.7	77.0	112.7	108.3	100.8
28–2–22; 31–2–22	59.6	58.1	79.9	89.7	84.2
34–2–22; 37–2–22	75.4	73.8	97.4	82.6	90.7
Dihedral angle (°)					
6–1–39–2	72.0	57.6	45.0	30.9	11.0
7–6–1–39	184.3	206.0	11.3	103.4	76.2
25–2–22–23	−4.1	1.2	−55.0	−106.6	−73.4
26–24–25–23	−77.5	−1.9	70.3	33.6	47.5
E_{rot} (a.u.)	−255.938 7	−255.776 1	−255.916 4	−255.805 8	−255.920 5

(5) $(CH_3F,11H_2O)$.—Calculations were performed for different C–F distances, from 1 to 10 Å, by keeping the fluorine atom on the C_3 axis of the methyl group. As in the previous calculations the geometry of the water molecules was kept rigid and partial local symmetries were retained. The number of water molecules included in these calculations is the sum of those in the first solvation shell of the separated ions. It is noteworthy that this number is very close to that found, namely 10—12, for the first solvation shell of CH_3F on the basis of structural considerations and thermodynamic evidence.[5]

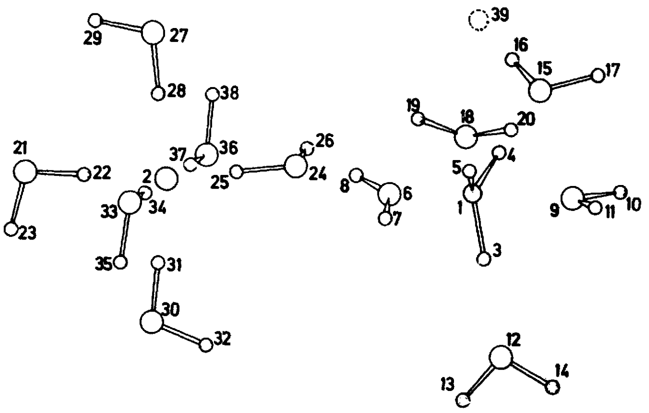


FIGURE 3 Numbering of atoms, definining the optimized geometrical parameters for the $(CH_3F,11H_2O)$ system. The dotted circle represents an imaginary reference atom. Atom 39 lies in the plane of the paper, *i.e.* in the plane 1–2–3. The angle 2–1–39 is 90°

Within such approximations, 16 geometrical parameters have been optimized for each C–F distance. These 16 variables are defined by means of internal co-ordinates of the system, seven distances, five angles, and four dihedral angles, identified by means of numbers assigned to atoms, as shown in Figure 3. The list of the variables, the energy and the geometrical data evaluated at the most significant C–F distances are summarized in the Table. The other variables have been fixed according to the following

---

[13] W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 1971, **93**, 808.

[14] H. Kistenmacher, H. Popkie, and E. Clementi, *J. Chem. Phys.*, 1974, **61**, 799.

assumptions. The three C–H bonds were assumed equal and fixed at a value of 1.118 Å; one of the water molecules along the C–H directions was placed in the plane of the drawing, and the others were obtained from this by ±120° rotation around axis 1—2. The O(9) atom is on axis 1—2 and its water molecule lies in the plane perpendicular to the drawing. The direction 1—6 was taken as the symmetry axis for the water molecule with O(6). For the molecules with oxygens 21, 24, 27, 30, 33, and 36 O–H bonds pointing towards the fluorine (atom 2) were assumed along with the respective F···H directions. O(21), O(27), and O(30) water molecules were kept in the plane of the drawing, and O(33) and O(36) in the plane 9–10–11. The planes 35–33–34 and 37–36–38 are perpendicular to 9–10–11.

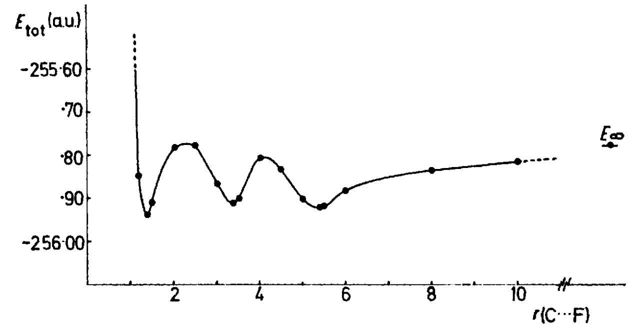


Figure 4 Total energy *versus* C–F distance for ($CH_3F,11H_2O$)

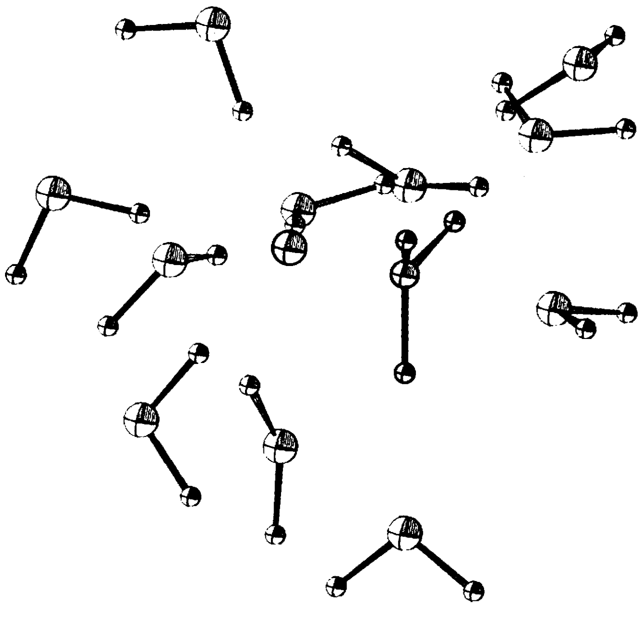


Figure 5 Molecular packing of ($CH_3F,11H_2O$) for the energy minimum at 1.388 Å

The trend of total energy *versus* C–F distance is shown in Figure 4. The structures of the supermolecule corresponding to the three minima [r(C–F) 1.388, 3.480, and 5.463 Å] are drawn in Figures 5—7. These figures have been obtained by means of the ORTEP computer program.[15]

DISCUSSION

The present results must be interpreted by keeping in mind that the CNDO method systematically overestimates bonding properties; with this view the short hydrogen bond distances and the anomalous behaviour of the FCH angle for a few molecular packings can be rationalized.

The most important point of the present calculation is the curve of the total energy of the supermolecule *versus* the C–F distance, where three well established minima, corresponding to three different species, are clearly present.

It would be tempting to compare these species with Scheme 1 which reflects the current interpretation of experimental data.[1-4] But it must be kept in mind that Scheme 1 is the result of studies on a number of systems, with different organic substrates, solvents, nucleophilic reagents, influence of normal, common ion, or special salts, *etc.*, while our calculations refer just to the model system ($CH_3F,11H_2O$).

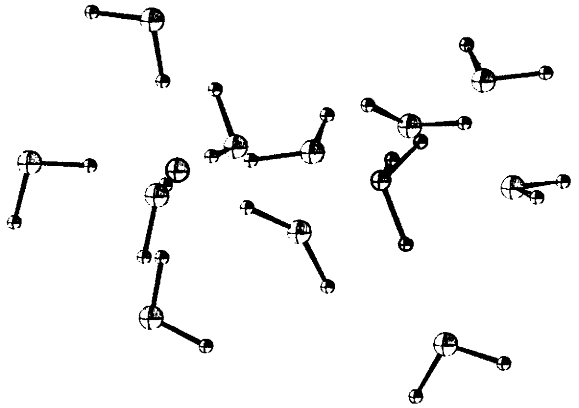


Figure 6 Molecular packing of ($CH_3F,11H_2O$) for the energy minimum at 3.480 Å

The first minimum at a C–F distance of 1.388 Å corresponds to the ' covalent ' R–X molecule in solution. Due to solvation the geometry is slightly different from that of the isolated molecule [r(C–F) 1.344 Å], and the negative charge on F is increased from —0.185 to —0.255. The water molecules are arranged in such a

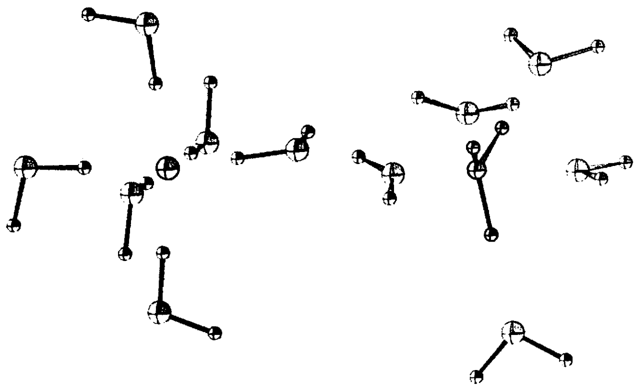


Figure 7 Molecular packing of ($CH_3F,11H_2O$) for the energy minimum at 5.463 Å

---

[15] C. K. Johnson, ORTEP, Oak Ridge National Laboratory, Oak Ridge, 1969.

way to build a cage surrounding the solute molecule as shown in Figure 5.

An increase of the C–F distance leads to a second energy minimum at 3.480 Å. The position of solvent molecules is changed. There are now two water molecules close to the C–F bond, each one with an O–H bond almost parallel to C–F direction, the hydrogen pointing towards the fluorine. The location of these and remaining water molecules is shown in Figure 6. The negative charge on fluorine is increased to −0.516.

Further extension of the C–F bond allows two water molecules to enter into the region between C and F atoms (see Figure 7) and a third minimum is found at *r*(C–F) 5.463 Å. The two ions are now in two different but adjacent solvent cages. This situation corresponds to dissociated ions, since each ion in the ion pair is completely surrounded by solvent molecules, occupying relative positions very similar to those of solvated ions at infinite separation. The negative charge on fluorine is −0.531, to be compared with the value of −0.568 found in $(F,6H_2O)^-$.

Further increase of the C–F distance is parallelled by an increase in energy, since we are now separating two charged species and working against coulombic attraction. The asymptotic value of the energy is the sum of energies of the two hydrated ions.

From the general shape of the curve in Figure 4 it can be argued that the three species have comparable stabilities and are separated by barrier heights of chemical significance. However the geometrical features of the intermediates have only indicative significance, since for each cluster many configurations with nearly the same energy are present at the reaction temperature.

In conclusion the present results, based on an extremely crude model and carried on by means of a simple MO treatment, show an agreement with experimental data and suggestions,[3,4] as good as could be hoped for. Indeed the available kinetic data for solvolysis and nucleophilic reactions for CH_3F in water[3] have been interpreted on the basis of Scheme 2, that is with the

$$CH_3F \rightleftharpoons CH_3^+F^- \longrightarrow CH_3OH + F^-$$

SCHEME 2

assumption that dissociation of CH_3F in water occurs through the intervention of at least one type of ion pair.

We suggest that more extensive (namely a number of different substrates) and more sophisticated (*i.e.* allowing bond making as well as bond breaking to occur) calculations should be able to contribute significantly to the understanding of the mechanism of nucleophilic substitution and solvolytic reactions in polar solvents. However the present results represent the most detailed description, namely the only one based on a molecular model, for ion pairs in solution available at the moment. We believe they give a faithful qualitative representation of the mechanism by which CH_3F molecules dissociate in water.

[6/126 *Received*, 19*th January*, 1976]