Theoretical Study of the Mechanism of Solvolysis of Methyl Fluoride

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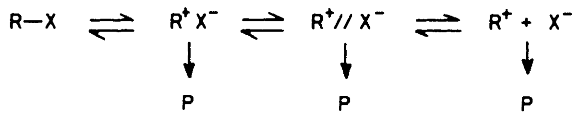
The mechanism of solvolysis of methyl fluoride has been studied by the CNDO/2 method using different numbers of water molecules. It is shown that the process implies the transfer of one proton through a chain of water molecules. The results obtained give theoretical support to Winstein's mechanism and demonstrate that solvent assistance to the carbocation in formation is a very important factor in the ionization part of the process.

According to Ingold,[1,2] solvolysis reactions, a special case of nucleophilic substitution reactions, can take place through two different mechanisms. In the S_N2 mechanism, the reaction occurs in only one step and there takes place inversion of configuration. On the other hand, in the S_N1 mechanism, a rapid product-controlling step is thought to follow a slow rate-determining ionization of RX to a cationic intermediate, thus implying racemization. In general, it was accepted that those molecules with a minimal number of alkyl substituents at the carbon atom undergoing substitution conform to the S_N2 mechanism, while those with considerable substitution at this carbon exhibit the usual characteristics of the S_N1 mechanism.

Apart from these extreme cases, there are borderline reactions which do not clearly correspond to any of the two above mentioned mechanisms. Traditional explanations for this borderline behaviour generally assumed one of two forms,[3,4] either direct competition between distinct S_N1 and S_N2 processes, or a new hybrid mechanism with intermediate characteristics. From the kinetic study of several solvolysis reactions, Winstein[5] concluded that the attempt to describe the solvolysis of borderline substances in terms of two different simultaneous processes was not successful, while the description in terms of one process accounts for all the known facts. The mechanism proposed by Winstein is outlined in the Scheme.[6,7]



Scheme.

According to this mechanism, solvolysis always takes place through the presence of at least one intermediate. If this intermediate is the solvent-separated ion pair (II) or the dissociated ions (III), both retention or inversion of configuration are possible, in good agreement with the prediction of the S_N1 mechanism. On the other hand, if the reaction takes place through the intimate ion pair (I), only inversion of configuration is possible, and in this case the results agree with the characteristics of the S_N2 mechanism. Thus, the mechanism proposed by Winstein is unifying in the sense that it permits an explanation of the entire spectrum of mechanistic types, S_N1, borderline, and S_N2.[8] However, the existence of ion pair intermediates in the solvolysis of methyl halides has recently been shown to be unnecessary,[9] thus questioning the unifying character of Winstein's mechanism.

In a theoretical CNDO/2 study[10,11] of the dissociation of methyl fluoride solvated with 11 water molecules, three energetic minima for three different values of the C–F distance were found. These minima corresponded closely to the covalent structure, to the intimate ion pair, and to the solvent-separated ion pair, respectively. This study seemed to give theoretical support to Winstein's mechanism. However, it has to be noted that the geometries of the water molecules were not optimized and, therefore, the results obtained for the dissociation reaction are difficult to apply to the solvolysis.

In subsequent theoretical work, Dannenberg,[12,13] using the idea of solvent assistance,[14] suggested that the intermediates considered by Winstein *et al.* might better be described as anion stabilized intermediates (ASI) and anion–cation stabilized intermediates (ACSI) rather than intimate and solvent-separated ion pairs, respectively.

The mechanism of solvolysis of methyl halide has been the subject of great controversy. Traditionally, this reaction was considered as a typical example of the S_N2 mechanism, the most difficult to include in the unifying scheme. The object of this paper is to make a more complete study of the solvolysis of methyl fluoride, using a variable number of water molecules and the CNDO/2 method. In this study we do not impose any restriction on the geometry optimization. In this way, it should be possible to clarify the existence or not of any intermediate in the process, and the nature of these intermediates where they do exist.

Methods

Given the impossibility of making a complete calculation of the potential hypersurface, a good approximation consists in taking one or two geometrical parameters as independent variables in order to reduce the dimension of the potential hypersurface. For each set of values of the independent variables, all the remaining geometrical parameters of the system are optimized.

The computations have been performed with the aid of the GEOMO program.[15] The geometry has been optimized by means of a variable metric method, using the analytical procedure proposed by Rinaldi and Rivail[16] for gradient computation. Since our aim was to carry out the optimization of the molecular geometry without any restriction, the semiempirical CNDO/2 method[17] has been employed, for it allows the calculations to be carried out within reasonable limits. It should also be mentioned that recent work by Simonetta[18] validates this use of CNDO/2 by showing that the *ab initio* energy profile for the dissociation of fluoromethane in hydrofluoric acid shows qualitatively the same shape as the CNDO profile. On the other hand, the possible use of the semiempirical MINDO/3 method has been rejected because this method appears to be unreliable for hydrogen bonded systems.[19]

Table 1. Potential barriers and stabilization energies of the solvated reactant for the solvolysis of methyl fluoride [a]

	Retention		Inversion	
N [b]	$\Delta E^{\ddagger}$	ΔE_s [c]	$\Delta E^{\ddagger}$	ΔE_s [c]
1	281.2	−30.5		
2	123.4	−81.6		
3	95.4	−147.7	87.4	−124.3
4	77.4	−207.1	58.2	−191.6
5	75.3	−263.6	65.3	−245.6

[a] Energy values in kJ mol^{-1}. [b] Number of water molecules. [c] Referred to the isolated molecules.

Table 2. Bond lengths [a] and net charges [b] for solvated methyl fluoride [c]

	$N = 3$		$N = 4$		$N = 5$	
	R	I	R	I	R	I
C–F	1.36	1.36	1.36	1.37	1.36	1.37
C–O	1.66	1.92	1.64	1.80	1.63	1.76
q_F	−0.23	−0.23	−0.23	−0.25	−0.23	−0.27
q_{CH_3}	+0.15	+0.22	+0.13	+0.25	+0.13	+0.26

[a] In Å. [b] In a.u. [c] R and I stand for retention and inversion, respectvely.

Results and Discussion

Using the C–F distance as independent variable, the energetic profiles of the solvolysis of methyl fluoride with different numbers of water molecules, placed in different positions, have been calculated. Table 1 presents the results obtained when the water molecules are placed in a chain, the extremes of which are situated on the carbon and fluorine atoms. Except in the cases of one and two water molecules, in which it is not possible to form a chain long enough to study inversion of configuration, in all other cases we have studied this process takes place as well as retention.* In Table 1, $\Delta E^{\ddagger}$ represents the potential barrier for the solvolysis and ΔE_s represents the stabilization energy of methyl fluoride when it is solvated with a chain of N water molecules, this stabilization energy being referred to the sum of energies of the isolated molecules.

Comparing the $\Delta E^{\ddagger}$ values, it can be observed that the potential barrier diminishes by increasing the number N of water molecules which make up the chain. This diminution is attenuated upon increasing N, showing practically no change in going from $N = 4$ to 5 when the retention of configuration is considered, but a slight increase in the barrier in the case of inversion. It is also noteworthy that the barriers of inversion are smaller than those of retention. However, given that the differences are not important, both processes can be expected to take place. The reason for the diminution of the potential barrier upon increasing the number of water molecules is due to the intervention of the chain of water molecules in the process. As can be seen in Figure 1, the process consists essentially in a progressive reorganization of the chain, through which one proton is transferred from the water molecule which attacks the methyl group to the fluorine atom.[20]

In all cases, the process occurs in one step, the presence of intermediates not being detected. However, when one compares the ΔE_s values for retention and inversion, it is remarkable that the stabilization of methyl fluoride in retention is always greater than that for inversion, although, as we have indicated previously, the latter always has a smaller potential barrier. This striking fact seems to indicate that in the whole process, although taking place in one step, there must be a factor, differentiated from nucleophilic attack itself, which will initially favour the retention of configuration.

In order to find out what this factor is, we present in Table 2, for N = 3—5, the net charges on the fluorine atom and on the methyl group, and the bond lengths C–F and C–O, O being the oxygen atom of the water molecule which attacks the methyl group. Two important facts can be observed. First, the C–O distance is smaller in retention than in inversion, which means that the methyl group is solvated more efficiently when its configuration is retained. Secondly, although the net charges on F and CH_3 are almost equal and opposite in sign in inversion, the net charge on CH_3 is much smaller than that on F in retention, the remainder of the positive charge being now delocalized over the chain of water molecules. Therefore, in retention there is more important solvent assistance to the carbocation in formation, which implies greater stabilization. So, we can conclude that the factor which initially favours the retention of configuration is just this greater stabilization of the methyl fluoride ionization in the retention process.

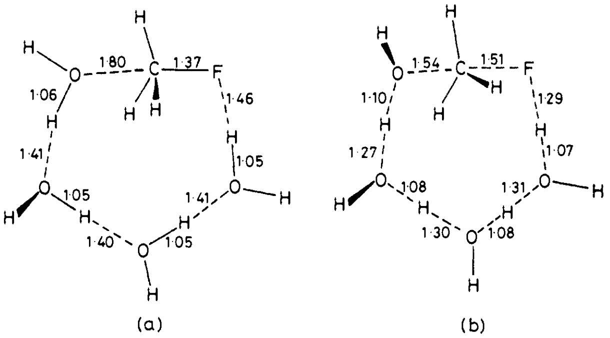


Figure 1. Structures of the reactant (a) and transition state (b) for the solvolysis of methyl fluoride solvated by four water molecules. Only the inversion of configuration is depicted (bond lengths in Å)

From the results presented in Table 2, it is clear that in solvolysis there exists an ionization phase which can be differentiated from nucleophilic attack, and that this ionization is very important in the initial part of the reaction. In this way, the whole process can be easily understood. Although ionization favours retention of configuration at the beginning of the process, nucleophilic attack takes place with inversion of configuration because the C–F bond breaks up more easily in this case.

In order to obtain a deeper insight into the real importance of ionization and nucleophilic attack in solvolysis, it is interesting to consider one case in which retention and inversion of configuration may be competitive. We have thus studied the solvolysis of methyl fluoride solvated with eight water molecules, the most stable structure of the reactant being presented in Figure 2. In this structure, there is a chain of four water molecules producing inversion of configuration, a chain of three water molecules producing retention of configuration, and one water molecule solvating fluorine in such a way that this atom may achieve a tetrahedrical configuration.

The energy profile calculated for this solvolysis reaction is

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* Obviously, inversion or retention of configuration can only be detected experimentally when the groups linked to the carbon atom are different.

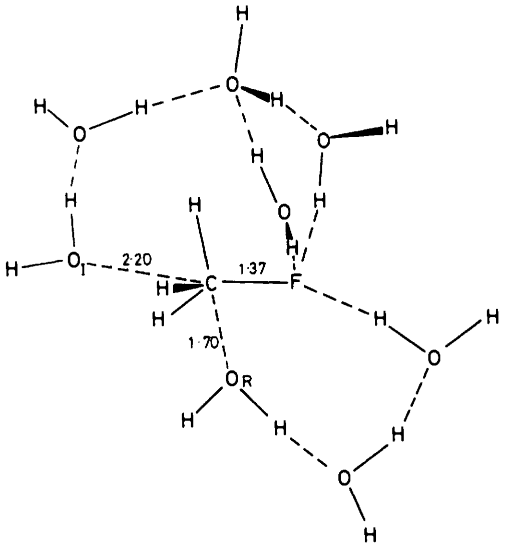

Figure 2. Structure of methyl fluoride solvated by eight water molecules (bond lengths in Å)

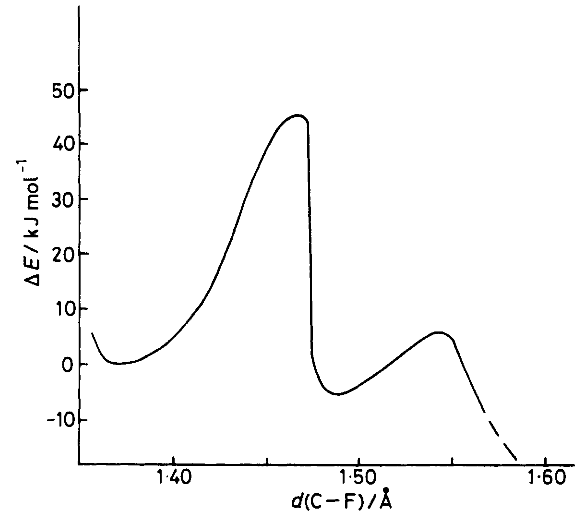

Figure 3. Energy profile for the solvolysis of methyl fluoride solvated by eight water molecules

presented in Figure 3. In this case, the process takes place through a two-step mechanism, although the second potential barrier is very small. The first potential barrier has a value of 44.0 kJ mol^{-1}, which is smaller than those obtained previously with only one chain of water molecules. The intermediate has a C–F distance of 1.48 Å and is slightly more stable than the reactant itself.

Table 3 presents for the reactant, transition states, and intermediate, the net charges on the fluorine atom and on the methyl group, the C–F distance, and the distances between the carbon atom and the oxygen atoms of the nearest water molecules in the inversion and retention chains. Comparing the two C–O distances, it can be observed that, for the reactant, the C–O_R distance is much smaller than that of C–O_I, thus implying that the water molecule of the retention chain solvates methyl fluoride in a more stabilizing way than does the water molecule of the inversion chain, in good agreement with the results obtained with only one chain of water molecules. For the first transition state, the C–O_R distance is still notably smaller than C–O_I. On the other hand, for the intermediate, both distances remarkably diminish and they become equal. This fact is a consequence of the important solvent assistance to the carbocation in formation, as can be deduced from the values of the net charges. In fact, while the absolute value of the charges on F and on CH_3 are equal in the reactant, the intermediate shows an important delocalization of charge over the chains of water molecules, because the charge on F has increased and the charge on CH_3 has become negligible. Finally, for the second transition state, the C–O_I distance is already smaller, showing that nucleophilic attack is performed by the water molecule of the inversion chain, thus explaining the inversion of configuration of the methyl group. Our calculations have also shown that it is a hydrogen atom of the inversion chain which is linked to the fluorine atom on the other end of the chain. The results obtained with eight water molecules prove that ionization and nucleophilic attack are not only two different aspects of the whole process, but also that their relative importance greatly varies for each step of the reaction. Consequently, the first step consists essentially in an ionization process, while in the second step the true nucleophilic attack is produced.

Table 3. Bond lengths [a] and net charges [b] for the reactant, intermediate, and transition states of the solvolysis of methyl fluoride solvated by eight water molecules

	C–F	C–O_I	C–O_R	q_F	q_{CH_3}
Reactant	1.37	2.20	1.70	−0.24	0.25
TS1	1.47	1.91	1.63	−0.31	0.25
Intermediate	1.48	1.53	1.53	−0.40	0.01
TS2	1.54	1.48	1.52	−0.44	−0.02

[a] In Å. [b] In a.u.

The results obtained in this paper agree quite well with Winstein's mechanism. However, the calculated intermediate does not strictly correspond to an intimate ion pair, but it still has a covalent, although highly polar, structure. The fundamental result is that this highly polar intermediate is strongly stabilized by solvent assistance to the carbocation in formation.

Our calculations have been done with a limited number of water molecules and, therefore, they do not explain the great complexity of a solution process. However, we believe that they do permit several important conclusions on the mechanism of solvolysis to be reached. First, the potential barrier of the solvolysis reaction is greatly diminished through the intervention of chains of water molecules. Secondly, we have given theoretical support to the validity of Winstein's scheme for the solvolysis of methyl fluoride, a reaction which has generally been considered as a typical example of an S_N2 process. We have found that even in this case it is possible to distinguish two steps: an ionization phase followed by nucleophilic attack of the highly polar intermediate by the solvent. Finally, we have confirmed that solvent assistance to the ionization process is a fundamental aspect of solvolysis. However, instead of the generally admitted solvent assistance to the anion,[12,13] we have found that solvent assistance to the carbocation is much more important, the cation stabilization being a favourable factor for the nucleophilic attack itself.

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