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On a Possible Catalytic Effect of Water on Some Nucleophilic Substitution Reactions in "Inert" Solvents

Giuliano Alagona, Eolo Scrocco and Jacopo Tomasi

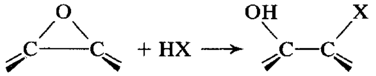
Laboratorio di Chimica Quantistica ed Energetica Molecolare del C.N.R., Via Risorgimento, 35, I-56100 Pisa, Italy

Ab initio SCF MO LCAO calculations with the 4-31G basis set on the ten most stable complexes involving H_2O, HF, HCl, F^- and Cl^- have been examined in order to verify whether there is some evidence supporting the hypothesis that water can act as a catalyst for some nucleophilic substitution reactions performed in inert solvents with hydrogen halides as nucleophile agents (e.g. the formation of halohydrins from epoxides). Energetic considerations and an analysis of the electrostatic contribution to the reactivity of the H_2O–HX adduct seem to support this hypothesis.

Key words: Heterolytic cleavage – Catalytic effects – Hydrogen bonded complexes

1. Introduction

Several authors have studied hydrogen-bonded complexes involving H_2O, HF, HCl, F^- and Cl^- by *ab initio* molecular orbital methods in order to deduce a physical model for the hydrogen bond [1–3]. We consider in this paper the same complexes from a different point of view, namely whether one can get some information on a possible catalytic effect of water in "inert" solvents to enhance the capability of the hydrohalic acids HX to attack organic substrates in reactions generally considered nucleophilic substitutions, an example of which is given by the formation of halohydrins from epoxides:



(1)

In the present study we shall not consider a specific case of reactions of this kind and do not discuss the details of the reaction mechanism, as we have done in preceding investigations [4] but, rather, we shall pay attention to the changes of the energy of the heterolytic cleavage of the HX bond: $HX \rightarrow H^+ + X^-$ produced by the formation of dimers $HX \cdot HX$ or, in presence of small quantities of water, by the formation of complexes $H_2O \cdot HX$.

The physical model assumed in this paper consists thus of hydrohalic acid and water molecules dispersed in a medium which, to simplify matter, is considered as completely inert. Only at the level of discussion we shall consider also the presence of the organic substrate.

Within this model of the solution we shall consider firstly the associative interaction between two molecules:

$$H_2O + HX \longrightarrow H_2O \cdot HX \tag{2}$$

$$2\,HX \longrightarrow HX \cdot HX \tag{3}$$

These association processes may be followed by a set of heterolytic cleavages schematized in the following equations:

$$H_2O \cdot HX \longrightarrow H_2OX^- + H^+ \tag{4}$$

$$H_2O \cdot HX \longrightarrow H_3O^+ + X^- \tag{5}$$

$$HX \cdot HX \longrightarrow HX_2^- + H^+ \tag{6}$$

$$HX \cdot HX \longrightarrow H_2X^+ + X^- \tag{7}$$

which may be in competition among themselves. We shall compare the changes of internal energy ΔE_i of such processes with the ΔE_0 value of the direct cleavage:

$$HX \longrightarrow H^+ + X^- \tag{8}$$

defining as "catalytic effect" of the second partner involved in the reaction (HX or H_2O) the differences $\delta_i = \Delta E_i - \Delta E_0$, where the subscript i refers to the reactions (4–7).

2. Results and Discussion

A good representation of the energetics of the reactions leading to a cleavage of a covalent bond can be obtained only by making use of wave-functions of high quality, suitable to reproduce the substantial rearrangements of the electronic distribution, the modification of geometry and the changes in correlation energy.

We have limited our calculations at the SCF level, using a small basis set, the 4-31G one [5]. This level of accuracy is at present the best obtainable if one wishes to make predictions for reactions similar to those considered in this paper, but having as "catalyst" a molecule by far more complex than H_2O or HX (ranging from the usual Friedel-Crafts catalysts, like BF_3 or $AlCl_3$, to the enzymatic ones). We shall examine later whether such relatively crude calculations are sufficient to evidence the main features of the catalytic effect we are searching for. For the sake of consistency, an optimization of geometry for all the molecular species was performed, and the main results (geometry, total energy, association energy, dipole moment, Mulliken's gross atomic charges) are reported in Table 1. The Fig. 1 gives a sketch of the molecular geometries of the species $H_2O \cdot HX$, H_2OX^- and $HX \cdot HX$ and the definitions of the geometrical parameters used in Table 1.

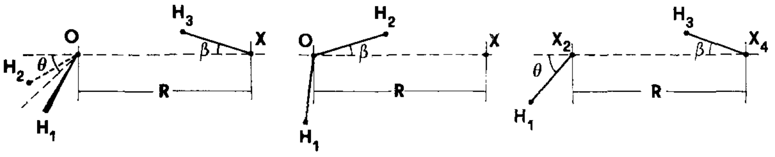


Fig. 1. Geometry and atom numbering of the $H_2O \cdot HX$, H_2OX^- and $HX \cdot HX$ complexes

Starting from the energies reported in Table 1 one can extract the changes of internal energy ΔE_i which are summarized in Fig. 2 and which constitute the basis for the present discussion.

It turns out evident, as expected, that the formation of the complexes facilitates the release of a proton from the halogenic acid by lowering the corresponding ΔE_i value: for HF in the presence of water we found $\delta_4 = -28.0$ kcal/mole and for HCl $\delta_4 = -11.6$ kcal/mole. The parallel association of the halogenic acid to give

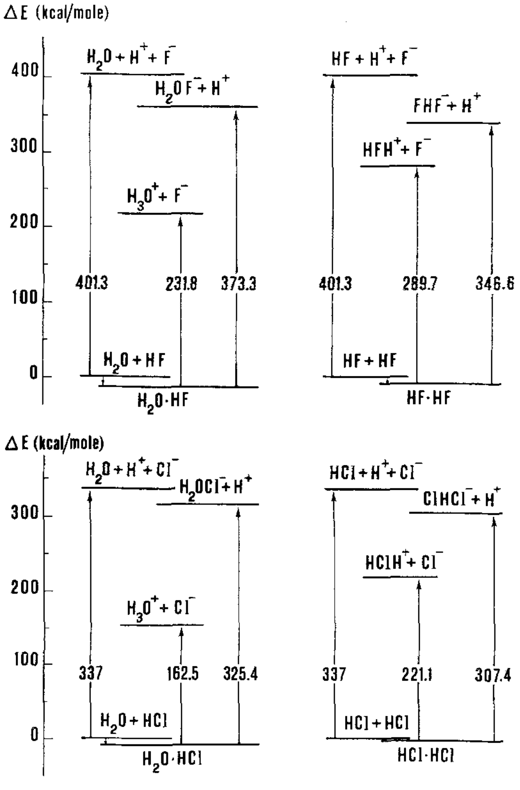


Fig. 2. Diagrams of the energies involved in reactions (2–8) as they result from the present computations

Table 1. 4-31G Geometries, total energies, association energies, dipole moment and Mulliken's gross atomic charges

	Geometry[a]	Energy[b]	E_A^c	Dipole[d]	Charge[e]
H_2O	$r_{OH}=0.952$ $H\hat{O}H=111.5$	-75.9086		2.48 (1.85)[f]	$q_H= 0.4022$ $q_O=-0.8045$
H_3O^+	$r_{OH}=0.964$ $HOH=120$	-76.2006	-183.2		$q_H= 0.5836$ $q_O=-0.7507$
F^-		-99.2478			$q_F=-1$
HF	$r_{HF}=0.922$[g]	-99.8873		2.29 (1.82)[f]	$q_H=-q_F=0.4792$
H_2OF^-	$r_{OH_1}=0.958$[h] $r_{OH_2}=1.05$ $r_{OF}=2.416$ $H_1\hat{O}H_2=108.7$ $\beta=4.04$	-175.2229	-41.7		$q_{H_1}= 0.3091$ $q_{H_2}= 0.5024$ $q_O=-0.9726$ $q_F=-0.8389$
$H_2O\cdot HF$	$r_{OH_1}=r_{OH_2}=0.95$[h] $r_{H_3F}=0.939$ $r_{OF}=2.610$ $H_1\hat{O}H_2=112.5$ $\beta=3.69$ $\theta=32.27$	-175.8178	-13.7	5.33 (3.7)[i]	$q_{H_1}=q_{H_2}=0.4370$ $q_{H_3}= 0.5357$ $q_O=-0.8342$ $q_F=-0.5755$
HFH^+	$r_{HF}=0.969$ $H\hat{F}H=125.5$	-100.0779	-119.6		$q_H= 0.6666$ $q_F=-0.3332$
FHF^-	$r_{HF}=1.146$ $F\hat{H}F=180$	-199.2350	-62.7		$q_H= 0.5590$ $q_F=-0.7795$
$HF\cdot HF$	$r_{H_1F_2}=0.925$[h] $r_{H_3F_4}=0.927$ $r_{FF}=2.69$ $\beta=8.15$ $\theta=56.2$	-199.7873	-7.96	4.35 (2.99)[l]	$q_{H_1}= 0.5063$ $q_{H_3}= 0.5022$ $q_{F_2}=-0.4754$ $q_{F_4}=-0.5330$
Cl^-		-459.0264			$q_{Cl}=-1$
HCl	$r_{HCl}=1.301$	-459.5634		1.87 (1.08)[f]	$q_H=-q_{Cl}=0.2314$
H_2OCl^-	$r_{OH_1}=0.958$[h] $r_{OH_2}=0.977$ $r_{OCl}=3.112$ $H_1\hat{O}H_2=106.6$ $\beta=13.3$	-534.9675	-20.4		$q_{H_1}= 0.3563$ $q_{H_2}= 0.4281$ $q_O=-0.8879$ $q_{Cl}=-0.8965$
$H_2O\cdot HCl$	$r_{OH_1}=r_{OH_2}=0.95$[h] $r_{H_3Cl}=1.326$ $r_{OCl}=3.129$ $H_1\hat{O}H_2=115.3$ $\beta=2.07$ $\theta=25.7$	-535.4860	-8.8	5.39	$q_{H_1}=q_{H_2}=0.4358$ $q_{H_3}= 0.3114$ $q_O=-0.8222$ $q_{Cl}=-0.3609$
$HClH^+$	$r_{HCl}=1.325$ $H\hat{Cl}H=101.5$	-459.7514	-118		$q_H=0.4140$ $q_{Cl}=0.1719$

	Geometry[a]	Energy[b]	E_A^c	Dipole[d]	Charge[e]
$ClHCl^-$	$r_{H\dot{C}l}=1.610$ $Cl\hat{H}Cl=180$	-918.6404	$-\ 31.7$		$q_H=\ 0.2691$ $q_{Cl}=-0.6346$
$HCl \cdot HCl$	$r_{H_1Cl_2}=1.299$[h] $r_{H_3Cl_4}=1.301$ $r_{ClCl}=3.986$ $\beta=7.04$ $\theta=75.2$	-919.1302	$-\ 2.13$	3.21	$q_{H_1}=\ 0.2474$ $q_{H_3}=\ 0.2414$ $q_{Cl_2}=-0.2271$ $q_{Cl_4}=-0.2618$

Experimental values are given in parentheses.
[a] Bond lengths in Å.
[b] Hartrees.
[c] Association energy in kcal/mole.
[d] Debyes.
[e] e units $=4.803 \times 10^{-10}$ e.s.u.
[f] Ref. [47].
[g] Ref. [48].
[h] Geometrical parameters defined in Fig. 1.
[i] Ref. [49]. See also Ref. [14].
[l] Ref. [23].

a dimer is still more effective: the δ_6 values for releasing a proton are -54.7 kcal/mole for HF and -29.6 kcal/mole for HCl. It must be remarked that other substances are more effective: for example in a recent paper [6] we have shown that complexation of HF with BF_3 gives $\delta=-119$ kcal/mole for the releasing of the proton (result obtained with the same methodology and the same basis set as the one used in the present paper).

If one pays attention to the processes leading to the formation of an anion X^- (Eqs. (5) and (7) compared to (8)) one can ascertain that the complexation is even more effective ($\delta_5=-169.5$ kcal/mole and $\delta_7=-111.6$ kcal/mole for HF, $\delta_5=-174.5$ and $\delta_7=-115.9$ kcal/mole for HCl). In fact the lowering of the energy obtained by process (5) with respect to that required in process (8) is due to the energy gain for the formation of the H_3O^+ ion (-183.2 kcal/mole in the 4-31G basis set calculations) and that found in process (7) with respect to (8) is due to the proton affinity of HX (which results to be -119.6 kcal/mole for HF and -118.0 kcal/mole for HCl). Process (5) results thus to be the most effective in producing a heterolytic cleavage, and the catalytic effect of small quantities of water in facilitating reactions of the type considered in the introduction has been confirmed.

The first point to discuss concerns the reliability of the relative magnitudes of the δ values for the various reactions.

The results of Fig. 2 should be compared with analogous calculations of higher quality[1] or with reliable experimental results. Unfortunately there is not, to the best of our knowledge, a complete set of results at a uniform level of accuracy, which may act as a reference standard for a check. Nevertheless from the data available in the literature, although incomplete, some useful information can be extracted especially in view of extending this investigation to larger catalysts.

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[1] Minimal basis set calculations are not sufficiently reliable for such a kind of analysis. We report, to permit comparisons, the δ values obtained with a STO-3G basis set for the HF case: $\delta_4=-101.8$, $\delta_5=-221.3$, $\delta_7=-177.2$ kcal/mole.

For the aim of the present paper it is sufficient to restrict our attention to the values of the association energy and to the importance of the variations in geometry arising from association. The complexes of Table 1 can be divided into three categories: complexes between two neutral molecules, complexes between a neutral molecule and an anion, and protonated species. For the first set of complexes, the importance of the variation of geometry can be checked by comparing our results with those reported by Topp and Allen [7] and by Kollman *et al.* [8] which refer to 4-31G calculations performed with rigid internal geometries and optimization only of two conformational parameters. As can be seen from Table 1 a complete optimization does not produce significant changes in the internal geometries. Optimization of the angle measuring the non-linearity of the H bond gives values ranging from 2.1° in $H_2O \cdot HCl$ to 7° in $HCl \cdot HCl$. The corresponding energy changes are only a few tenths of a kcal/mole.

The HF·HF dimer has been largely studied [7–20]. We report in Table 2 a selection of results giving a total energy equal or better than that of Table 1. An enlargement of the basis set produces a lowering of the association energy. From the results of Lischka [19] one can deduce that in the HF dimer the correlation corrections play a minor role. The value of the dimerization energy given by Ref. [19], which when corrected for the zero-point vibration becomes −2.90 kcal/mole, is too low compared to the experimental estimates [21–23]. The reason for this discrepancy is partly due to the assumption of a linear geometry of the dimer in the calculations, the other factor being an unbalancement of the basis set due to the

Table 2. Results for $(HF)_2$ taken from the literature

Basis set	Method	$E_{\text{tot}}{}^{a}$	E_A^b	R^c	θ^c	β^c	Ref.
4-31G	SCF	−199.78733	−8.0	2.69	55.9	8.1	[13]
6-31G	SCF	−199.97877	−7.5	2.71	53.5	8.2	[13, 14]
[3*s*, 1*p*/1*s*]	SCF	−199.99647	−4.6	2.88	20	(0)	[15]
6-31G*	SCF	−200.01543	−6.0	2.72	81	16	[13]
6-31G**	SCF	−200.03289	−6.0	2.72	80	15	[13]
[4*s*, 2*p*/2*s*, 1*p*]	SCF	−200.03726	−6.5	2.78	20	(0)	[15]
[5*s*, 3*p*/3*s*]	SCF	−200.04926	−6.4	2.78	(0)	(0)	[16]
6-311G*	SCF	−200.08938	−4.7	2.81	65	9	[13]
[4*s*, 2*p*, 1*d*/2*s*, 1*p*]	SCF	−200.0953	−4.6	2.80	52.2	(0)	[17]
[5*s*, 4*p*, 1*d*/3*s*, 1*p*]	SCF	−200.11989	−4.5	2.85	40	(0)	[18]
[7*s*, 4*p*, 2*d*/4*s*, 1*p*]	SCF	−200.13074	−3.5	2.90	(0)	(0)	[19]
	HFAO + CI	−200.01845	−5.3	2.88	(0)	(0)	[20]
	PNO(CI)	−200.54462	−3.5	2.87	(0)	(0)	[19]
	CEPA	−200.57761	−3.5	2.89	(0)	(0)	[19]
	IEPA	−200.67541	−3.4	2.895	(0)	(0)	[19]
Experimental		—	−7 ± 1	2.79	72		[21, 22]
			−6 ± 1.5		40 ± 5		[23]

[a] Hartrees.

[b] Kcal/mole.

[c] Geometrical parameters defined in Fig. 1; distances in Å, angles in degrees. The unoptimized parameters are within parentheses. The geometry optimization is complete only in the first case.

limitation in the polarization *d* functions which are more effective in describing the monomer electron distribution. The more reliable computations seem to be those of Diercksen and Kraemer [18] and of Curtiss and Pople [13]. For the other neutral H-bonded complexes it is not possible to perform such comparisons. In $H_2O \cdot HF$ the inclusion of polarization functions (6-31G* basis set [24]) lowers the association energy to -9.2 kcal/mole. To the best of our knowledge there are no larger basis set calculations for $H_2O \cdot HCl$ and for $HCl \cdot HCl$ (for STO-3G and 4-31G calculations see Refs. [8, 10]) and the only experimental result available is for the dimerization energy of HCl (-2.14 ± 1 kcal/mole [25]). Such comparisons, supported by a few ones for other dimers, are sufficient to draw a few conclusions: 1) The SCF 4-31G calculations for the first row dimers exaggerate the stabilization energy, for the second row dimers such a trend is reversed or at least greatly reduced [9, 26]. 2) Corrections for correlation energy changes are not essential. 3) Optimization of geometry can be limited to a couple of conformational parameters.

In complexes between a neutral molecule and an anion the errors of the 4-31G calculations are larger because of the difficulty in describing a negative ion using a limited basis set SCF calculation. Results better than ours are reported in Table 3.

The association with the fluoride ion does not produce relevant changes in the internal geometry of water [32]. Changes in the correlation energy contribute for nearly 2 kcal/mole to the association energy of H_2OF^- [34]. The best values of

Table 3. Results for the dimers including X^- taken from the literature

Basis	Method	$E_{tot}{}^a$	E_A^b	R^c	Ref.
		FHF^-			
[4*s*, 2*p*/2*s*]	SCF	−199.53781	−53	2.246	[29]
[5*s*, 3*p*/2*s*, 1*p*]	SCF	−199.55478	−40	2.25	[27]
STO-DZ+*d*+*f*	SCF	−199.57296	−27	2.22	[28]
	CI	−199.77860	−56	2.246	[29]
Experimental			−58 ± 5		[30]
			−37		[31]
		H_2OF^-			
[5*s*, 4*p*, 1*d*/5*s*, 4*p*, 1*d*/3*s*, 1*p*]	SCF	−175.54093	−24.07	2.41	[32]
[5*s*, 4*p*, 1*d*/5*s*, 4*p*,1*d*/3*s*, 1*p*]	SCF	−175.54121	−24.22 (−21.04)	2.509	[34]
[7*s*, 4*p*, 2*d*/4*s*, 3*p*, 2*d*/2*s*, 2*p*]	SCF	−175.5560	−23.7 (−22.2)	2.514	[33]
	CI	−175.95602	−26.16 (−22.98)	2.471	[34]
Experimental			−23.3		[35]
		H_2OCl^-			
STO-DZ	SCF	−535.2340	−19.5	3.04	[36]
[9*s*, 6*p*, 2*d*/4*s*, 3*p*, 2*d*/2*s*, 2*p*]	SCF	−535.6503	−11.9 (−11.4)	3.31	[33]
Experimental			−13.1		[35, 38]

[a] Hartrees.

[b] Kcal/mole. In parentheses values corrected for the molecular extra correlation energy and for zero-point vibrational energy.

[c] Distances in Å defined in Fig. 1. The geometry optimization is partial in all the cases here reported.

Refs. [33] and [34], after correction for the zero-point vibration energy (−22.2 and −22.98 kcal/mole, respectively), are in good accord with the experimental value of Ref. [35]. An analogous good agreement with the experimental value shows the computation of Kistenmacher *et al.* [33] for the affinity of Cl^- with water. After correction for the zero-point energy and the correlation changes the value of the enthalpy of formation of H_2OCl^- is −11.4 kcal/mole.

Less good is the agreement with the experimental values for FHF^-. The results of Støgard *et al.* [29] seem to be in better agreement with an earlier estimate of the association energy [30] (the correction for the zero-point vibration is in this case less than 1 kcal/mole) than with a more recent value [31].

For $ClHCl^-$ there are no large SCF or CI calculations available to check the two experimental values proposed for the association energy: −14.2 [37] and −24 [38] kcal/mole.

The last set of molecular species to be considered are the three cations H_3O^+, H_2F^+ and H_2Cl^+. Calculations using an extended basis for H_3O^+ [34] give the following E_A values: −174.3 (SCF) and −172.8 (CI) kcal/mole, which corrected for the zero-point vibration energy changes led to the following proton affinities of water: −169.0 (SCF) and −167.5 (CI), to be compared with the experimental estimates: -166 ± 2 [39] and -168 ± 3 [40] kcal/mole. Corrections to the 4-31G value for the zero-point vibration energy give a proton affinity of −177 kcal/mole.

Estimates of the proton affinity of HF from experimental measurements decreased in the last years from −137 [41] to −116 kcal/mole (M. S. Foster and J. L. Beauchamp, private communication, quoted by Refs. [42, 43]). For HCl we know only an old experimental estimate of -141 ± 3 kcal/mole [44]. Calculations for H_2F^+ give values of the proton affinity in the range of −114 kcal/mole (nonoptimized geometry with a [4*s*, 2*p*/2*s*] basis set [42]), of −117.2 kcal/mole (optimized geometry on a [5*s*, 3*p*/2*s*] basis [45]), and of −123.3 kcal/mole with the 6-31G** basis [43].

There are not, to the best of our knowledge, sufficiently reliable calculated values of the proton affinity of HCl to decide whether the experimental value of Ref. [44] is overestimated.

To conclude these comparisons, we have collected in Fig. 3 a selection of the best experimental or calculated values to be compared to the 4-31G values of Fig. 2. In order to make comparisons easier, the values reported in Fig. 3 do also refer to the bottom of the corresponding potential surfaces. This selection is to some extent a question of choice, and surely some particular points could be revised. For this reason we have not reported the uncertainty range of such estimates.

The reader may constate that in spite of numerically significant deviations, the relative ordering of the δ_i values is essentially the same in the two sets of data.

Returning to the chemical problem mentioned in the introduction we discuss the meaning and usefulness of the results of Fig. 2 or of other more accurate values. It should be clear that the determination of the δ values constitutes only a first step

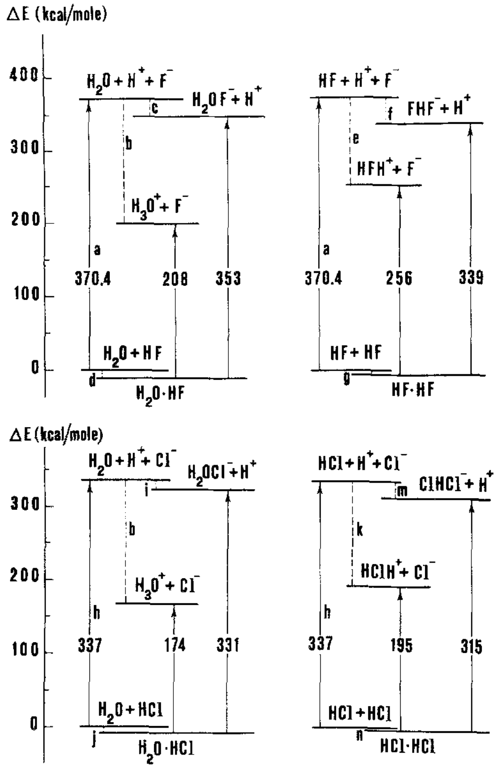
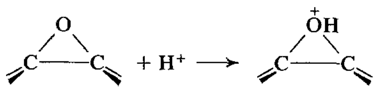


Fig. 3. Diagrams of the energies involved in reactions (2–8) deduced from experimental measurements or from other calculations. The data we have employed derive from the following sources: a) heterolytic dissociation of HF: *E*(HF) from Ref. [50], *E*(F^-) from Ref. [51]. Another value (369.3 kcal/mole) can be deduced from Refs. [52] and [53]; b) proton affinity of H_2O from Ref. [39]: another value (-168 ± 3 kcal/mole) is given in Ref. [40]; c) from Ref. [38]; d) from Ref. [14] (calculated value with a 6-31G* basis set); e) proton affinity of HF quoted in Refs. [42, 43], an older value (-137 kcal/mole) is given in Ref. [41]; f) from Ref. [31], another value (-58 ± 5 kcal/mole) is given in Ref. [30]; g) from Refs. [21, 22]; h) heterolytic dissociation of HCl: from Refs. [54] and [53]. Another value (333.3 kcal/mole) can be deduced from Refs. [52] and [53]; i) from Ref. [35]; j) from Ref. [8] (calculated with a 4-31G basis set); k) from Ref. [44]; m) from Ref. [38], another value (-14.2 kcal/mole) is given in Ref. [37]; n) from Ref. [25]

in the assessment of the question. Even in a schematic model of the solution, as that used here, other physical processes may occur, like associations of the intermediate species with other molecules of the solution, which may cooperate in reducing the amount of energy necessary to break the H–X bond. But rather than a speculation on possible refinements of the description of the processes occurring in the solution, we prefer reconsidering the actual example of formation of halohydrins from epoxides which actually constitutes the first motivation for the present study.

The actual mechanism of reaction (1) depends upon experimental conditions. It is generally agreed that in protic media the first, fast, step of reaction is given by a protonation of the epoxide: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followed by an attack of the conjugated acid II by X^- [46]. Little is known about the actual mechanism of reaction (1) in anhydrous aprotic media. Measurements of the electric conductivity, performed in our laboratory with different substrates and solvents, clearly brought out that reaction (1) can arrive at completion without formation of electrically charged species. More refined calorimetric measurements [56] seem to indicate that the reaction under anhydric conditions can be catalysed by small amounts of water.

If water is absent, or present only in catalytic quantities, it may be possible that instead of an actual heterolytic cleavage of HX preceding the attack of the substrate, a more complex concerted mechanism involving also the epoxide molecule occurs. In the present paper we have considered processes where the epoxide is not present, but the comparison of the energies of the reactions (4–8) maintains some usefulness also in the case of concerted processes because it gives information on the relative weight of a contribution to the reaction energy barrier which can lead to a distinction among several possible reaction paths.

The possibility of a catalytic action of water on the reaction (1) via process (5) could open new perspectives to the detailed description of the mechanism of this reaction in inert solvents. In a yet unpublished *ab initio* investigation of the potential energy surface for reaction (1) ($X=F$) we have adopted a model consisting of a molecule of oxirane and a molecule of HF only. Within this model we have found a marked preference for a path leading to a fluoridrine with retention of configuration, instead of an alternative path leading to a fluoridrine with inversion of configuration. If the process can proceed through the intermediate of Eq. (2) or Eq. (3), some steric strains to this reaction (which can be reduced to the concomitant cleavage of two bonds: H–F and C–O) should be eliminated and the channel leading to an inversion of configuration should be deepened.

Moreover, one can add some hints suggesting that $H_2O \cdot HF$ might be more reactive than HF in the initial phase of this reaction. For this purpose we compare in Fig. 4 the electrostatic potential[2] V of HF and $H_2O \cdot HF$ along two straight lines in the outer part of the molecular space, the first running in the $M \rightarrow H$ direction (where M is F in HF and O in $H_2O \cdot HF$) and sampling the electrostatic potential in the region near the H atom (in the $H_2O \cdot HF$ the H_1 atom of Fig. 1), the second one running in the $H \rightarrow F$ direction and sampling V in the region near the F atom. As is well known, V gives a fairly reliable indication for the reactivity of a molecule as far as the initial stages of the reaction are concerned. A more positive value of V corresponds to a larger electrophilic character, and a more negative value to a larger nucleophilic character of the atom or group in the region where V is sampled. From Fig. 4 it turns out that $H_2O \cdot HF$ has a larger reactivity than HF either if the reagent approaches the epoxide with its electrophilic or with its nucleophilic end. The raising of V in the region of H due to the formation of the complex with water is decidedly lower than the corresponding raising one has with more efficient catalyst, like BF_3 (see Fig. 2 of Ref. [6]). It can be remarked, in

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[2] The classical electrostatic potential of a molecule M is given by

$$V_M(k) = \int \gamma(1) \frac{1}{r_{1k}} d\tau_1$$

Where $\gamma(1)$ is the total (electronic and nuclear) charge distribution of the molecule M [55].

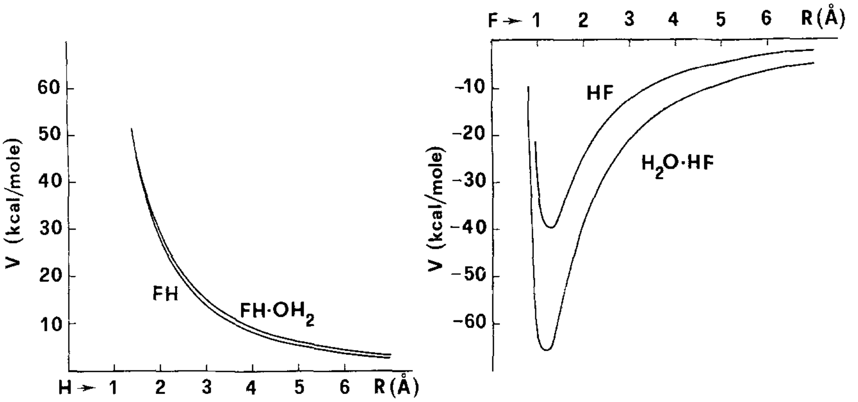

Fig. 4. Comparison of the electrostatic potential of HF and $H_2O \cdot HF$ along some selected straight lines: a) a line running along the F → H bond in HF and along a O → H bond in $H_2O \cdot HF$. The distances are measured from the H atom, b) a line running along the H → F bond in HF and in $H_2O \cdot HF$. The distances are measured from the F atom

addition, that in this case the examination of the Mulliken's gross atomic charges (Table 1) would have led to opposite conclusions. The lowering of V in the regions near the F atom is appreciably larger (attention could be focussed, for example, on the point at 3 Å from F: V is -12 kcal/mole for HF and -21.2 kcal/mole for $H_2O \cdot HF$) and this fact could facilitate to some extent an approach of the reagent leading to a direct attack of F to the oxirane molecule. This approach as said before, turns out decidedly unfavoured in the case of the reaction between $(CH_2)_2O$ and HF compared to the alternative one involving the H atom of the reagent. The same conclusions can be reached in the case of the HCl and $H_2O \cdot HCl$ (see Fig. 5).

Of course it is not possible from the schematic representation of V given in Figs. 4 and 5 to obtain the actual values of the electrostatic interaction energy between reagent and oxirane. Anyway such description seems to us sufficient to indicate that one can add the analysis of the electrostatic reactivity of the reagents to the other arguments (steric considerations and catalytic effects on the heterolytic cleavage of the HX bond) which suggest that complexation of the hydrohalic acid with water should facilitate the formation of halohydrins from epoxide in "inert" solvents.

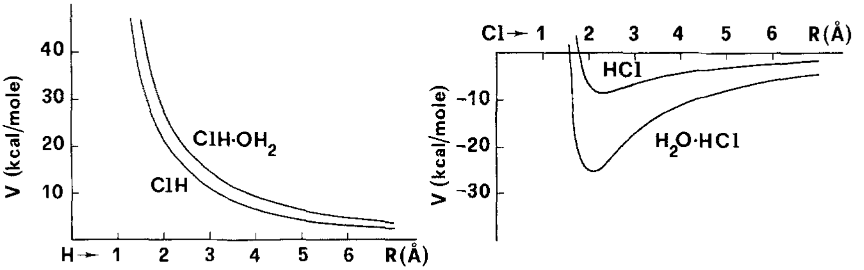

Fig. 5. Comparison of the electrostatic potential of HCl and $H_2O \cdot HCl$. Same remarks as in Fig. 4

References

1. Joesten, M. D., Schaad, L. J.: Hydrogen bonding. New York, N.Y.: M. Dekker 1974
2. Kollman, P. A., Allen, L. C.: Chem. Rev. **72**, 283 (1972)
3. Pimentel, G. C., McClellan, A. L.: Ann. Rev. Phys. Chem. **22**, 347 (1971)
4. Alagona, G., Scrocco, E., Tomasi, J.: J. Am. Chem. Soc. **97**, 6976 (1975)
5. Ditchfield, R., Hehre, W. J., Pople, J. A.: J. Chem. Phys. **54**, 724 (1971)
6. Silla, E., Scrocco, E., Tomasi, J.: Theoret. Chim. Acta (Berl.) **40**, 343 (1975)
7. Topp, W. C., Allen, L. C.: J. Am. Chem. Soc. **96**, 5291 (1974)
8. Kollman, P. A., McKelvey, J., Johansson, A., Rothenberg, S.: J. Am. Chem. Soc. **97**, 955 (1975)
9. Johansson, A., Kollman, P. A., Rothenberg, S.: Theoret. Chim. Acta (Berl.) **29**, 167 (1973)
10. Kollman, P. A., Johansson, A., Rothenberg, S.: Chem. Phys. Letters **24**, 199 (1974)
11. Lathan, W. A., Curtiss, L. A., Hehre, W. J., Lisle, J. B., Pople, J. A.: Progr. Phys. Org. Chem. **11**, 175 (1974)
12. Del Bene, J. E., Pople, J. A.: J. Chem. Phys. **55**, 2296 (1971)
13. Curtiss, L. A., Pople, J. A.: J. Mol. Spectry. **61**, 1 (1976)
14. Dill, J. D., Allen, L. C., Topp, W. C., Pople, J. A.: J. Am. Chem. Soc. **97**, 7220 (1975)
15. Kollman, P. A., Allen, L. C.: J. Chem. Phys. **52**, 5085 (1970)
16. von Niessen, W.: Theoret. Chim. Acta (Berl.) **31**, 297 (1973)
17. Yarkony, D. R., O'Neil, S. V., Schaefer III, H. F., Baskin, C. P., Bender, C. F.: J. Chem. Phys. **60**, 855 (1974)
18. Diercksen, G. H. F., Kraemer, W. P.: Chem. Phys. Letters **6**, 419 (1970)
19. Lischka, H.: J. Am. Chem. Soc. **96**, 4761 (1974)
20. Allen, L. C., Kollman, P. A.: J. Am. Chem. Soc. **92**, 4108 (1970)
21. Franck, E. U., Meyer, F.: Z. Elektrochem. **63**, 571 (1959)
22. Dyke, T. R., Howard, B. J., Klemperer, W.: J. Chem. Phys. **56**, 2442 (1969)
23. Smith, D. F.: J. Mol. Spectry. **3**, 473 (1959)
24. Hehre, W. J., Ditchfield, R., Pople, J. A.: J. Chem. Phys. **56**, 2257 (1972)
25. Rank, D. H., Sitaram, P., Glickman, W. A., Wiggins, T. A.: J. Chem. Phys. **39**, 2673 (1963)
26. Allen, L. A.: J. Am. Chem. Soc. **97**, 6921 (1975)
27. Noble, P. N., Kortzeborn, R. N.: J. Chem. Phys. **52**, 5375 (1970)
28. McLean, A. D., Yoshimine, M.: Tables of linear molecule wave functions. San Jose, Calif.: IBM Research 1967
29. Støgard, A., Strich, A., Almlöf, J., Roos, B.: Chem. Phys. **8**, 405 (1975)
30. Waddington, T. C.: Trans. Faraday Soc. **54**, 25 (1958)
31. Harrell, S. A., McDaniel, D. H.: J. Am. Chem. Soc. **86**, 4497 (1964)
32. Diercksen, G. H. F., Kraemer, W. P.: Chem. Phys. Letters **5**, 570 (1970)
33. Kistenmacher, H., Popkie, H., Clementi, E.: J. Chem. Phys. **59**, 5842 (1973)
34. Diercksen, G. H. F., Kraemer, W. P., Roos, B. O.: Theoret. Chim. Acta (Berl.) **36**, 249 (1975)
35. Arshadi, M., Yamdagni, R., Kebarle, P.: J. Phys. Chem. **74**, 1475 (1970)
36. Piela, L.: Chem. Phys. Letters **19**, 134 (1973)
37. McDaniel, D. H., Vallée, R. E.: Inorg. Chem. **2**, 996 (1963)
38. Yamdagni, R., Kebarle, P.: J. Am. Chem. Soc. **93**, 7139 (1971)
39. Cotter, R. J., Koski, W. S.: J. Chem. Phys. **59**, 784 (1973)
40. Chong, S. L., Myers, R. A., Franklin, J. L.: J. Chem. Phys. **56**, 2427 (1972)
41. Beauchamp, J. L., Holtz, D., Woodgate, S. D., Patt, S. L.: J. Am. Chem. Soc. **94**, 2798 (1972)
42. Johansson, A., Kollman, P. A., Liebman, J. F., Rothenberg, S.: J. Am. Chem. Soc. **96**, 3750 (1974)
43. Pople, J. A., Binkley, J. S.: Mol. Phys. **29**, 599 (1975)
44. Haney, M. A., Franklin, J. L.: J. Phys. Chem. **73**, 4329 (1969)
45. Wild, U. P., Ha, T. K., Raggio, G. A., Keller, H. U., Brunner, P. O.: Helv. Chim. Acta **58**, 696 (1975)
46. Lamaty, G., Malog, R., Selve, C., Sivade, A., Wylde, J.: J. Chem. Soc. Perkin II, 1119 (1975)
47. Nelson, R. D., Lide, D. R., Maryott, A. A.: U.S. Dept. Com., Nat. Bur. Std., NSRDS-NBS 10 (1967)
48. Lathan, W. A., Hehre, W. J., Curtiss, L. A., Pople, J. A.: J. Am. Chem. Soc. **93**, 6377 (1971)

49. Bevan, J. W., Legon, A. C., Millen, D. J., Rogers, S. C.: Chem. Commun. **130**, 341 (1975)
50. Cade, P. E., Huo, W. M.: J. Chem. Phys. **47**, 614 (1967)
51. Clementi, E., McLean, A. D.: Phys. Rev. **133A**, 419 (1964)
52. Selected values of chemical thermodynamic properties, NBS Technical Note N. 270–3. Washington, D.C.: U.S. Government Printing Office 1968
53. Berry, R. S.: Chem. Rev. **69**, 533 (1969)
54. Cade, P. E., Huo, W. M.: J. Chem. Phys. **47**, 649 (1967)
55. Scrocco, E., Tomasi, J.: Topics Curr. Chem. **42**, 95 (1973)
56. Bellucci, G., Berti, G., Ingrosso, G., Vatteroni, A., Ambrosetti, R., Conti, G.: to be published

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