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CONFORMATIONAL ANALYSIS OF 2-HALOETHANOLS AND 2-METHOXYETHYLHALIDES IN A PHOTOELECTRON-SPECTROMETER

THE INTERPRETATION OF SPECTRA BY "AB INITIO" CALCULATIONS

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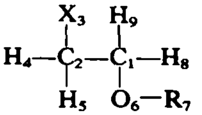
Abstract—The photoelectron spectra of 2-haloethanols and 2-methoxyethylhalides have been interpreted by "ab initio" calculations. The results support the hypothesis that, in vapor phase, fluoride and chloride derivatives exist only in one rotameric form: the *gauche* form for the alcohols and the planar *trans* form for the ethers. In case of bromo and iodo compounds both forms coexist.

Studies by different analytical methods (IR, raman, microwave and electron diffraction) have indicated that, with the possible exception of fluoroethanol, the 2-haloethanols exist in two rotameric forms, a *gauche* form and a planar *trans* form. The percentage of each of those forms depends on the phase (vapor, in solution or liquid) on halogen and mostly on temperature (1–6 and refs. cited).

Photoelectron spectra of haloethanols have been recorded by Baker *et al.*,[7] 2-Iodoethanol and 2-methoxyethyliodide have been analysed by Leavell *et al.*,[8] In each case the different conformations of the compound have been neglected in the interpretation of the spectra.

In this paper the *ab initio* MO calculations indicate that 2-haloethanols **1** and 2-methoxyethylhalides† **2** exhibit *characteristical properties of their conformations* in their photoelectron spectra.



$$H_4-\underset{H_5}{\overset{X_3}{C_2}}-\underset{O_6-R_7}{\overset{H_9}{C_1}}-H_8$$

(1) R = H
(2) R = CH_3
X = F, Cl, Br, I

The energy of molecular orbitals (MOs) and the interactions between atomic or MOs have been estimated by *ab initio* calculations. Two species of interactions are differentiated as through space and through bond.

In general, through space interaction refers to interaction resulting from the direct overlap between non neighbouring orbitals of same symmetry, containing n or π electrons.[9]

Through bond interaction in a MO results in a delocalisation of two electrons over several bonds. This interaction in first approximation exhibits the inductive effect.

The simplest compounds to examine are the chlorine derivatives with which we began our study. Then we followed with the investigation of the fluorine derivatives and finally tried bromo and iodo compounds. The first bands in the photoelectron spectra of studied compounds have been assigned by comparison with those of corresponding to ethylhalides, ethanol and methylethylether.

Ethylhalides, ethanol and methylethylether

The energy, the main character and the symmetry of calculated MOs of sample references are listed in Table 1. The corresponding values† of vertical ionization potentials‡ (I.P.v) are also listed.

Our results are in good agreement with those taken from the literature except for ethylfluoride. The *ab initio* calculations show that the first two bands in the spectrum are the fluoride lone pair doublets while Yamazaki *et al.*,[11] have assigned these bands to σC—CA′ and πA″.

Experimental results and calculations

Photoelectron spectra of haloethanols and methoxyethylhalides have been recorded at room temperature with the 584 Å He resonance line. The resolution determined for Xenon bands was estimated to 0.025 eV.

The calculations were performed according to the *ab initio* MO method of Pople *et al.*,[12] using a minimal basis of Gaussian fitted slater-type orbitals (STO 3 G).

The geometries used for calculations were experimental values for fluoro and chloroethanol.[3,4]

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† To our best knowledge the 2-methoxyethylhalides (X = F, Cl and Br) spectra have not been reported.

† These values have been determined once more before the use.

‡ The values of the MO energies are consistent only with those of vertical ionization potentials according to the Koopmans' approximation.[10]

Table 1. IP's (eV) (I Exp), MO energies (eV) (I Calc), main characters K and symmetries S of orbitals.

Compound		I_1	K_1	S_1	I_2	K_2	S_2
EtOH	Exp	10.65	n O	A″	12.20	n O	A′
	Calc	9.49			10.79		
EtOMe	Exp	9.72	n O	A″	11.34	n O	A′
	Calc	8.96			10.34		
EtF[a]	Exp	12.43	n F	A′	12.87	n F	A″
	Calc	10.90			11.08		
EtCl	Exp	11.01	n Cl	A′	11.01	n Cl	A″
	Calc	10.17			10.22		
EtBr	Exp	10.28	n Br	$^2E_{3/2}$	10.60	n Br	$^2E_{1/2}$
EtI	Exp	9.34	n I	$^2E_{3/2}$	9.93	n I	$^2E_{1/2}$

[a] There is a linear combination between the atomic orbitals (AOs) containing the fluoride doublets and those of the neighbouring carbons with the same symmetry which leads to a splitting of first two degenerated levels of fluoride doublets.

The geometries of 2-methoxyethylfluoride and 2-methoxyethylchloride were estimated by combination of the values for alcohols and of the standard values reported in literature.[13]

For each compound the total energy computed for the first two stable conformers (*gauche* and *trans*) is given in Table 2.

The experimental values of IPs determined on the photoelectron spectra, the calculated energies of MO and their main character K are listed in Table 3.

The experimental results are not in very good agreement with the calculated ones because Koopmans' approximation is not satisfied for localised orbitals.[14] Furthermore, MO calculations have been computed with a minimal basis of Slater-type atomic orbitals and a standard value for the scaling factors. The energy values can be estimated using a more sophisticated basis set of AO and optimized scale factors. However, the related assignment of MO energy levels is satisfactory as well as the description of characters of every MO.

Chlorinated Compounds

(a) *Chloroethanol.* The most stable conformation of chloroethanol is a *gauche* conformation with H-bond (Table 2). A detailed study of calculated MO shows an overlaping between two AOs: the first one contains an oxygen doublet and the second one contains a chlorine doublet. This linear combination leads to:

(1) the formation of two bonding MOs where

Table 2. Total energies (a.u.) of trans and gauche conformations

Compound	Trans conformation	Gauche conformation with hydrogen bond	Gauche conformation without H. bond
FCH_2CH_2OH	−249.57147	−249.57542	−249.57290
FCH_2CH_2OMe	−288.15635	−288.14940	
$ClCH_2CH_2OH$	−606.12527	−606.12937	−606.12630
$ClCH_2CH_2OMe$	−644.71023	−644.70325	

Table 3. Experimental IP's (eV) (Exp) calculated energies for Gauche (Calc G) or Trans (Calc T) forms and MOs main characters of haloethanols and methoxyethylhalides.

Compound		I_1	K_1	I_2	K_2	I_3	K_3	I_4	K_4
FCH_2CH_2OH	Calc G	9.58	n O	10.86	n O	11.54	n F	12.41	n F
	Calc T	9.68		10.89		11.32		11.85	
	Exp	10.98		12.48		13.04		13.97	
FCH_2CH_2OMe	Calc G	9.08	n O	10.53	n O	11.26	n F	11.97	n F
	Calc T	9.25		10.68		11.27		11.38	
	Exp	10.18		11.94		12.68		13.00	
$ClCH_2CH_2OH$	Calc G	9.84	n O	10.59	n Cl	10.81	n Cl	11.45	n O
	Calc T	9.96		10.41		10.41		11.58	
	Exp	10.90		11.45		11.71		12.60	
$ClCH_2CH_2OMe$	Calc G	9.38	n O	10.28	n Cl	10.44	n Cl	11.03	n O
	Calc T	9.49		10.39		10.39		11.05	
	Exp	10.05		11.04		11.04		12.05	
$BrCH_2CH_2OH$	Exp G	10.75	n Br	10.93	n Br	11.30	n O		
	Exp T	10.65	$^2E_{3/2}$	10.83	$^2E_{1/2}$	11.30			
$BrCH_2CH_2OMe$	Exp G	10.13	n O	10.41	n Br	10.60	n Br		
	Exp T	10.20		10.51	$^2E_{3/2}$	10.76	$^2E_{1/2}$		
ICH_2CH_2OH	Exp G	9.73	n I	10.34	n I	10.96	n O		
	Exp T	9.60	$^2E_{3/2}$	10.17	$^2E_{1/2}$	10.96			
ICH_2CH_2OMe	Exp G	9.43	n I	10.03	n I	10.25	n O		
	Exp T	9.40	$^2E_{3/2}$	9.96	$^2E_{1/2}$	10.23			

one is the highest occupied MO (HOMO) MO 21 (69% n O−15% n Cl) whereas the second one is the MO 19 (75% n Cl+18% n O).

(2) the split of degeneracy of the levels containing the first two chlorine lone pair doublets that are nearly degenerated in alkylchlorides[15] since the effect of spin orbit coupling is very small ($\leq$0.07 eV).

For the same MOs, a weak interaction through bonds with adjacent methylenes increases the direct spatial overlap. MO 20 contains only the second chlorine lone pair doublet (92% n Cl).

By comparison with the reference spectra the first band of chloroethanol photoelectron-spectrum has been assigned to the ionisation from n electrons of oxygen lone pair and the second one to the ionisation from n doublets of chlorine. In fact, the intensity of the second band is double than that of the first band and the peak appears as a doublet. The difference between the two doublet tops is about 0.26 eV which is too large to be explained by a spin orbit coupling. This difference can be only accounted for by a splitting of levels containing chlorine lone pair doublets. Calculations have indicated that the splitting is possible only if there is a through space interaction. This through space interaction can occur only if the conformation of the compound is a gauche conformation.

All these results showed that: *in the gas phase the* gauche *form of chloroethanol is well preponderated.*

(b) 2-*Methoxyethylchloride.* Contrary to the chloroethanol the most stable conformation of the 2-methoxyethylchloride is a *trans* conformation (Table 2). In this case there is no through space interaction between oxygen and chlorine AOs. The through bond interactions are negligible and the two MOs formed with the first two chlorine doublets have the same energy (Table 3).

After comparison with methylethylether and ethylchloride the first band of methoxyethylchloride spectrum has been assigned to ionization from n oxygen electrons. The second band which is not splitted is twice intense compared to the first one and can be assigned to the ionization from two first chlorine electron doublets. From Table 3, it can be seen that the calculations are in good agreement with the experimental results. *Therefore, in gas phase the* 2-*methoxyethylchloride indicates to be in a* trans *conformation.*

Fluorinated compounds

In the case of fluoroethanol the most stable conformation calculated is a *gauche* conformation whereas 2-methoxyethylfluoride is a *trans* conformation (Table 2).

The comparison of results of the calculated MOs allows to explain the two fundamental differences between fluorinated and chlorinated compounds:

(1) whatever the conformation of fluoroethanol and methoxyethylfluoride may be, there is a linear combination between the AOs of oxygen and fluorine. This interaction occurs in this case between the AOs containing the *second* oxygen doublet and the first fluorine doublet.

The through space interaction is more important for the gauche fluoroethanol ($d_{O...F} = 2.42$ Å) than for the *trans* form of methoxyethylfluoride ($d_{O...F} =$ 3.63 Å).

(2) for the two compounds in *trans* or *gauche* conformation there is a strong through bond interaction between the AOs of fluorine and those of same symmetry of adjacent carbons. As in ethylfluoride this interaction is sufficient to split the degeneracy of the first two n_F MOs.

In these conditions it is possible that the spectrum of fluoroethanol may resemble that of 2-methoxyethylfluoride.

The first four bands of the photoelectron spectra of the two studied compounds have also been assigned by comparison with the reference spectra and with the calculated results. The first two bands are due to the ionization from the two n_O orbitals, the next two result from ionisation from the first two n_F MOs.

The difference of energy between the n_F MOs $\Delta I = I_4 - I_3$ (Table 3) is larger in fluoroethanol (1 eV) than in the 2-methoxyethylether (0.32 eV).

In the case of fluoroethanol, an important through space interaction increases the through bond interaction and extends the levels containing n_F doublets more than in the methoxyethylfluoride.

As in the ethylfluoride the splitting of degeneracy in methoxyethylfluoride comes essentially from the through bond interaction. The difference of energy between the first two n_F MOs is of same order of magnitude in ethylfluoride (0.44 eV) and in methoxyethylfluoride (0.32 eV). *Once more the photoelectron spectra reproduce well the conformation in gas phase of fluoroethanol and* 2-*methoxyethylfluoride.*

Brominated and iodinated compounds

The bromine and iodine derivatives cannot be computed by the chosen method of calculations. However, a thorough study of photoelectron spectra of these compounds is sufficient to determine their conformations. The assignments of the first bands of spectra have been accomplished experimentally as for previous derivatives. Bromoethanol, iodoethanol as well as 2-methoxyethyliodide facilitate the removal of a n halogen electron prior to an oxygen electron.

(a) *Bromine derivatives.* The bands assigned to ionization from the first two halogen doublets have two tops in both bromoethanol and 2-methoxyethylbromide. The split in two of the band of bromoethanol spectrum corresponding to the removal of a n oxygen electron is not apparent but it can be observed in the spectrum of methylether. The IP values are listed in Table 3. It is possible to assume that these compounds exist in both conformations gauche and trans in gas phase and at room temperature.

The following differences of energy in absolute value between the levels containing the first two bromine doublets are between 0.10 and 0.16 eV (Table 3). These differences are close to those measured ones for relatively unflexible *cis*- and *trans*-2-bromocyclopentanols (0.09 eV) and 2-methoxycyclopentylbromides (0.15 eV) (16). Since the distances between the substituants are nearly the same in these linear and cyclic compounds, this comparison is acceptable.

The interactions between bromine oxygen and the other atoms of the molecule are different for each compound and for each conformation. As a result the MOs have not the same energy in both cases and the first three bands of these compounds are split in two.

The bromine IP values have been assigned in the linear compounds to the true conformation by comparison with the corresponding values in the cyclic compounds (Table 4).

Table 4. IP's of bromine in linear and cyclic 2-haloalcohols and 2-methoxy alkylhalides (eV)

Compound	IP $Br_{3/2}$	IP $Br_{1/2}$	Conformation
2-bromocyclopentanol	10.10	10.37	trans
	10.19	10.49	cis
2-bromoethanol	10.65	10.83	trans
	10.75	10.93	gauche
2-methoxycyclopentyl-bromide	10.00	10.21	cis
	10.15	10.46	trans
2-methoxyethyl-bromide	10.41	10.60	gauche
	10.51	10.76	trans

Since the calculations for brominated compounds were not possible, the experimental values of bromine IP's have been compared with the calculated chlorine orbital energies. The values of energies performed for chlorine orbitals show the same inversion as the bromine IP's according to the chlorine conformation in the molecule and its association with OH or OCH_3. From the band intensities it is difficult to estimate the correct percentage in every one of the two conformations, but in first approximation they have the same probability.

(b) *Iodine derivatives*. The study accomplished for bromine derivatives can be applied to the iodinated compounds. The split in two of the bands corresponding to the ionization from n electrons of iodine provides a good explanation of the results of Franklin *et al.*,[8] The two rotamers coexist at 23° whilst at 200° the favoured conformation is probably the trans conformation.

Discussion concerning the hydrogen bond

It has been accepted that the *gauche* conformation, unstable *a priori* is favoured in presence of an intramolecular H-bond. But Griffith and Roberts[17] have implied that the H-bond is not necessary in order to observe a *gauche* conformation. To confirm this conception the calculations for fluoro and chloroethanol in the three following conformations have been carried out:

> a *trans* form A; a *gauche* form with the possibility of H-bond B (hydrogen of OH group is pointed towards halogen); a *gauche* form without the possibility of H-bond C (hydrogen of OH group is pointed towards the other side of the halogen).

The total energy E obtained for these three conformations (Table 2) are classified in this order: EB<EC<EA. This result shows that the hydrogen bond can effectively stabilize a gauche form, but its presence is not indispensable in order to observe a *gauche* conformation.

CONCLUSION

The photoelectron spectroscopy is a physical method which enables relatively easily to determine conformations of compounds in gas phase. Our results are in good agreement with those of Azrak *et al.*,[3,4] for fluoro and chloroethanol. This study confirms and explains the results of Franklin *et al.*[8] with iodinated compounds.

We have demonstrated that the *ab initio* method remains valid for the assignment of the principal bands in the photoelectron spectra.

EXPERIMENTAL

The GAUS 70 program of Hehre[18] has been used to carry out the calculations on an IBM 370/168 C.I.R.C.E. (ORSAY). The photoelectronic spectra have been registered on the Perkin-Elmer P.S. 16 in C.E.N. Saclay and the P.S. 18 in Ecole Polytechnique.

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