ELECTROSTATIC EFFECTS IN IONIZATION EQUILIBRIA: AN MNDO STUDY OF PROTON AND HYDROGEN TRANSFER REACTIONS OF 4-FLUOROBUTANOL

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MNDO molecular orbital calculations have been carried out for *sp* and *ap* conformers of 4-fluorobutanol and some 4-X-bicyclo[2.2.2]octanols (X = F, Cl). The results are analyzed in terms of substituent effects on proton transfer enthalpies $\delta \Delta H^0$ and homolytic bond dissociation energies $\delta DH^0(A-H)$ and compared with the previously reported data for 5-fluoropentanoic acid and 4-fluorobutylamine. The results are further compared with the prediction of the electrostatic theory. It is shown that the substituent polar effect F_D on the acidities of halogenoalcohols is largely due to substituent interaction in the anions and only to a smaller extent to interactions in the neutral alcohol. A small contribution (about one-tenth for the *ap* conformer) is probably also made by the substituent effects on homolytic bond dissociation energies $DH^0(A-H)$.

Electrostatic theory provides a useful framework upon which analysis of the substituent effects in proton transfer reactions may be based. Considering ionization equilibria in the gas phase,[1-3] the electrostatic theory developed by Smallwood[4] seems to be more appropriate than the generally adopted theory of Kirkwood and Westheimer.[5,6] The reason for this is the cancellation of all solvation terms: the effect of the dipolar substituent X is considered as the change of reaction enthalpy $\delta \Delta H^0$ of the isodesmic reaction (A) in the gas phase.

$$X\text{—}A\text{—}H + A^- \rightleftarrows X\text{—}A^- + A\text{—}H \qquad (A)$$
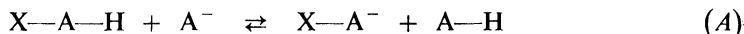
Provided that the effective relative permittivity ε_{ef} equals one for the gas phase, the electrostatic field effect F_D on the equilibrium (A) is expressed in both theories by the same equation

$$\delta \Delta H^0 \simeq \delta \Delta E^0 = Ze\mu \cos \Theta / (4\pi\varepsilon_0 r^2 \varepsilon_{ef}) , \qquad (1)$$

where Z is the charge valence (± 1), e the electronic charge, μ is the dipole moment

of substituent X, r the distance between charge Ze and the centre of the dipole moment μ, and Θ is the angle between vectors r and μ.

Use of Eq. (I) generally assumes that the remaining resonance R_π and steric S_D substituent effects have been eliminated by the proper choice of the system. However, as we reported in our previous papers,[7,8] two shortcomings of the theory still have not been adequately resolved. The homolytic bond dissociation energies $DH^0(\text{A--H})$ in the substituted and unsubstituted acids do not cancel and thus the difference $\delta DH^0(\text{A--H})$ can interfere in the reaction enthalpy $\delta\,\Delta H^0$, and the electrostatic field effect F_D can be considered both in the neutral acids X—A—H and in the charged anions X—A$^-$.

So far there are only very limited experimental data on the changes of $DH^0(\text{A--H})$ due to substitution in the gas phase[9−12] and/or in solution[13−15] experiments, and none of the available data deals with the $\cos\Theta/r^2$ dependence of the F_D effect. Similarly, there are only a few papers[16−20] that deal simultaneously with the alternative action of the F_D effect.

Recently, we tested the two assumptions of the electrostatic theory on the ionization equilibria of the conformers of 5-fluoropentanoic acid[7] and 4-fluorobutylamine.[8] For the reasons mentioned above, we decided to extend our previous test of the electrostatic theory at the semiempirical MNDO level to another type of organic acids — to structurally related halogenoalcohols. We chose the sp and ap conformers of 4-fluorobutanol (structure I) as model compounds, which allowed us to test the F_D effects of the carbon–fluorine dipole even for the different geometry parameters r and $\cos\Theta$ in Eq. (I). The applicability of the MNDO method was checked on the structurally related 4-substituted bicyclo[2.2.2]octanols (4-X-BCO, structure II).

I, sp I, ap $II, X = F, Cl$
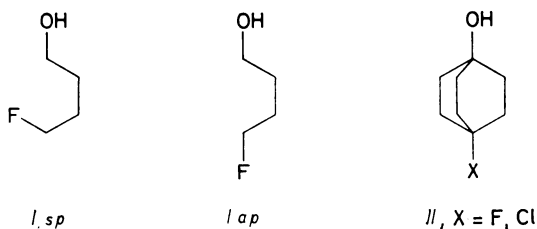
CALCULATIONS AND RESULTS

The quantum chemical calculations were made at the semiempirical MNDO level[21] by using the MNDO program.[22] The standard geometric parameters[23] were used as a starting value for the total geometry optimization. During the latter, the planar geometry of the carbon chain was kept for the two conformers of I, and the D_{3h} symmetry of the bicyclic skeleton was held in 4-substituted bicyclo[2.2.2]octanols. The doublet multiplicity was assumed for the X—A$^\bullet$ and A$^\bullet$ radicals.

The calculated enthalpies of formation ΔH_f^0 for all R—CH$_2$CH$_2$CH$_2$CH$_2$—X structures mentioned above and for 4-X-bicyclo[2.2.2]octanols are given in Table I. The net atomic charges on the hydroxyl proton q_H and the charges q_O on the oxygen atoms in the OH, O$^-$, and O$^\bullet$ groups are given in Table II.

Electrostatic Calculations

The relative electrostatic energies $\delta \Delta E^0$ were calculated from Eq. (*1*) using $\varepsilon_{ef} = 1$ and introducing the difference $\mu_X - \mu_H$ for μ. Standard bond moments[24] were used (in 10^{-30} C m): C—H, $-1\cdot0$ and C—F, $4\cdot67$. The geometry parameters r and $\cos \Theta$ were both calculated from the MNDO optimized atomic coordinates and from the standard geometric parameters.[23] In the second case, the ionizable proton of the hydroxyl group was located at a distance of 90 pm from the oxygen atom in the direction of the prolonged bond C—O. The negative charge on the hydroxyl anions was localized in both cases at the oxygen atom.

The electrostatic energies $\delta \Delta E^\circ$ were calculated taking charge valence $Z = +1$, while in the case of the relative electron affinities $\delta \Delta E^0(EA)$ the charge valence was taken as $Z = -1$. This means that $\delta \Delta E^0$ values express the energy change accompanying the removal of a proton from the neutral X—A—H molecule, while $\delta \Delta E^0(EA)$ predicts the energy of removal of an electron from the electrostatic field due to a substituent dipole in the anion X—A$^-$. The results are given in Table III.

DISCUSSION

As has been pointed out previously, the use of the MNDO method has several advantages for the study of proton transfer reactions in the gas phase.[7,8] In particular, the MNDO substituent effect estimates are at least as good as those obtained from the most widely used *ab initio* STO-3G calculations in the minimal basis set and without geometry optimization.[25-27] On the other hand we used neither the more sophisticated semiempirical AM1 method[28,29] nor the *ab initio* level[30,31] in order to preserve the compatibility with out previous results on the related X—CH$_2$CH$_2$. .CH$_2$CH$_2$—R model systems.[7,8]

The consistency of the MNDO calculated proton transfer enthalpies $\delta \Delta H^0$ and relevant STO-3G calculations,[25] which were derived from Eq. (*B*),

$$\text{X—A—H}_2^+ + \text{A—H} \rightleftarrows \text{X—A—H} + \text{A—H}_2^+ \qquad (B)$$
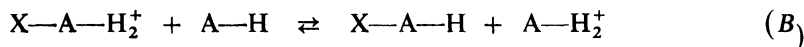
is reasonably good. In particular, the satisfactory agreement of $\delta \Delta H^0$ values of the *ap* conformer of *I* and 4-F-bicyclo[2.2.2]octanol (4-F-BCO, structure *II*) with the STO-3G calculation ($-22\cdot6$ and $-19\cdot0$ kJ mol^{-1} versus $-16\cdot6$ and $-16\cdot2$ kJ mol^{-1}, Table IV) suggests that MNDO provides proper description of the electrostatic F_D

effect on proton transfer reactions, because both alcohols have practically the same geometry parameters $\cos \Theta$ and r (see structure I), and thus the same theoretical magnitude of the F_D effect.

TABLE I

MNDO calculated enthalpies of formation ΔH_f^0 of the compounds $R-CH_2CH_2CH_2CH_2-X$, shown in Eq. (C) and some related bicyclic halogenoalcohols (in kJ mol^{-1})

X	Confor- mation	R^a		
		OH	O$^-$	O$^{\cdot}$
H	sp	$-272\cdot087$	$-198\cdot548$	$-27\cdot533$
	ap	$-282\cdot106$	$-207\cdot948$	$-45\cdot753$
F	sp	$-443\cdot907$	$-368\cdot454$	$-209\cdot060$
	ap	$-468\cdot456$	$-416\cdot882$	$-231\cdot434$
BCO^b		$-265\cdot997$	$-221\cdot710$	—
4-F-BCO		$-436\cdot013$	$-410\cdot683$	—
4-Cl-BCO		$-290\cdot764$	$-274\cdot163$	—

^{a} Data for compounds R = H taken from ref.^{8}; ^{b} BCO means bicyclo[2.2.2]octanol.

TABLE II

MNDO calculated net atomic charges of the compounds $R-CH_2CH_2CH_2CH_2-X$ and some related bicyclic halogenoalcohols (in electrons)

X	Confor- mation	$q_H{}^a$	$q_O{}^b$		
		R = OH	R = OH	R = O$^-$	R = O$^{\cdot}$
H	sp	$0\cdot1794$	$-0\cdot3287$	$-0\cdot7638$	$-0\cdot2250$
	ap	$0\cdot1789$	$-0\cdot3283$	$-0\cdot7644$	$-0\cdot2243$
F	sp	$0\cdot1780$	$-0\cdot3284$	$-0\cdot7653$	$-0\cdot2281$
	ap	$0\cdot1812$	$-0\cdot3247$	$-0\cdot7644$	$-0\cdot2243$
BCO		$0\cdot1816$	$-0\cdot3184$	$-0\cdot7188$	—
4-F-BCO		$0\cdot1816$	$-0\cdot3098$	$-0\cdot7116$	—
4-Cl-BCO		$0\cdot1823$	$-0\cdot3091$	$-0\cdot7046$	—

^{a} Net atomic charges on the hydroxyl proton; ^{b} net atomic charges on the oxygen atoms.

Unfortunately, it is not possible to compare calculated $\delta \Delta H^0$ of the *ap* conformer of *I* with the experimental value of its bicyclic analog 4-F-BCO, structure *II*, because only several aliphatic alcohols[32] and phenols[33,34] were investigated in the gas phase. As regards the data in solution, the solvolysis rate constants for 4-substituted bicyclo[2.2.2]octyl *p*-nitrobenzenesulfonates in 80% aqueous ethanol are available.[35] The derived $\delta \Delta G^0$ value for 4-Br-BCO $\left(-19 \cdot 0 \text{ kJ mol}^{-1}\right)$ is a reasonably good match with the $\delta \Delta H^0$ of 4-Cl-BCO in the gas phase $\left(-27 \cdot 7 \text{ kJ mol}^{-1}, \text{ Table IV.}\right.$

TABLE III
Relative electrostatic energies $\delta \Delta E^0$ and electron affinities $\delta \Delta E^0(\text{EA})$ of investigated halogeno-alcohols (in kJ mol^{-1})

Confor-mation	$\delta \Delta E^0$		$\delta \Delta E^0(\text{EA})$	
	MNDO[a]	Std.[b,c]	MNDO[a]	Std.[b]
Isp	6·9	17·3	−8·0	−27·0
Iap	−20·1	−15·5	25·6	22·1
4-F-BCO	−18·7	−15·5	24·4	22·1
4-Cl-BCO	−22·3	−18·5	29·4	26·3

[a] Geometry parameters cos Θ and r calculated from the MNDO optimized atomic coordinates;
[b] geometry parameters cos Θ and r calculated from the stadard geometric parameters (ref.[23]);
[c] positive charge localized at a distance of 90 pm from the oxygen atom in the direction of the prolonged bond C—O.

TABLE IV
Proton transfer enthalpies $\delta \Delta H^0$ and relative net atomic charges δq_H and δq_O of investigated halogenoalcohols

| Alcohol	$\delta \Delta H^0$	$\delta q_H{}^a$	$\delta q_O{}^b$	$\delta q_{O^-}{}^b$	$\delta q_{O\cdot}{}^b$
	kJ mol^{-1}	10^3 electron			
Isp	1·9	−1·4	0·3	−1·5	−3·1
Iap	−22·6[c]	2·3	3·6	10·4	8·2
4-F-BCO	−19·0[d]	0·0	8·6	7·2	—
4-Cl-BCO	−27·7	0·7	9·3	14·2	—

[a] Difference $q_H(X) - q_H(H)$; [b] difference $q_O(X) - q_O(H)$; [c] STO-3G calculated energy from Eq. (*B*) is $-16 \cdot 6 \text{ kJ mol}^{-1}$ (ref.[25]); [d] STO-3G calculated energy from Eq. (*B*) is $-16 \cdot 2 \text{ kJ mol}^{-1}$ (ref.[25]).

This decreasing trend in acidity agrees in general with the solvent attenuation factor[2] for the substituted phenols[33] (SAF(aq) $= \varrho_F(gas)/\varrho_F(aq) = 6.8$).

Comparison of the electrostatic theory with the MNDO calculations is presented in Tables III and IV. The problem is, likewise as in the case of previously studied carboxylic acids[7] and protonated amines,[8] whether the gas phase acidities $\delta\,\Delta H^0$ of halogenoalcohols are better predicted by the $\delta\,\Delta E^0$ or the $\delta\,\Delta E^\circ(EA)$ values. The data in Table III and IV show that both energies predict correctly the $\delta\,\Delta H^0$ value of the *ap* conformer of *I* but overestimate the reverse substituent effect in the *sp* conformer. No improvement is achieved by using the alternative location of the positive charge and standard geometry. We examined this problem by plotting the $\delta\,\Delta E^0$ and $\delta\,\Delta E^0(EA)$ values against the $\delta\,\Delta H^0$ energies of variable fluoroacids. This plot (in Fig. 1) shows that in the case of carboxylic acids and protonated amines the best fit is obtained with the MNDO geometry based $\delta\,\Delta E^0(EA)$ electron affinities. On the other hand, a slightly better fit of the $\delta\,\Delta H^0$ and electrostatic $\delta\,\Delta E^0$ energies can be seen for alcohols (points 2 and 6, Fig. 1). From this finding we can conclude that the $\delta\,\Delta H^0$ enthalpies are equally well approximated by the $\delta\,\Delta E^0$ and $\delta\,\Delta E^0(EA)$ MNDO energies in alcohols owing to a more distinct localization of the positive and negative charge.

In order to test the substituent effect both in neutral molecules of halogenoalcohols and in charged hydroxyl anions, the following three types of isodesmic reactions (C) were set up,
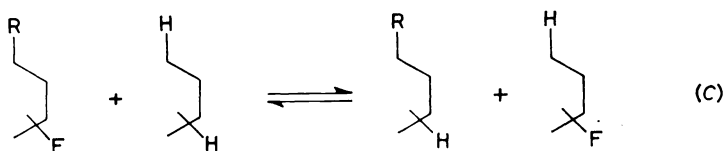
where R was either the hydroxy group OH, hydroxyl anion O^-, or hydroxyl radical $O^\bullet$ in both *sp* and *ap* conformers of 4-fluorobutanol. The substituent effect on acidity $\delta\,\Delta H^0$ (Table IV) is then given by the energy change for reaction (A), which is just the difference in $\delta\,\Delta H_C^0$ energies of the OH and O^- groups. In a similar way, the substituent effect on the homolytic bond dissociation energies $\delta DH^0(A-H)$ is given by the energy change for the reaction (D),

$$X-A-H + A^\bullet \rightleftarrows X-A^\bullet + A-H \qquad (D)$$
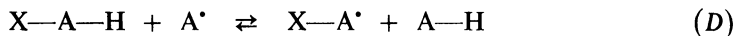
while Eq. (E) expresses the substituent effect on electron affinity of the radical $\delta\,EA(A^\bullet)$.

$$X-A^- + A^\bullet \rightleftarrows X-A^\bullet + A^- \qquad (E)$$
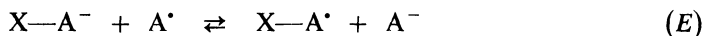
The total substituent effect on the gas phase acidity (proton transfer enthalpy) is then given with regard to reactions (A), (D), and (E) by Eq. (2):

$$\delta \Delta H^0 = \delta DH^0(A\text{–}H) - \delta EA(A^{\bullet}) \tag{2}$$

The MNDO calculated interaction energies $\delta \Delta H_C^0$, the homolytic bond dissociation energies $\delta DH^0(A\text{–}H)$, and electron affinities $\delta EA(A^{\bullet})$ are given in Table V. When comparing these data, it is obvious, that the predominant substituent effect on $\delta \Delta H^0$ is largely due to substituent interactions in the charged anion[17,20] and only to

TABLE V

MNDO calculated $\delta \Delta H_C^0$ energies of reaction (C), homolytic bond dissociation energies δDH^0. .(A–H) of reaction (D), and electron affinities $\delta EA(A^{\bullet})$ of reaction (E) (in kJ mol^{-1})

R	$\delta \Delta H_C^0$		δDH^0(A–H)		$\delta EA(A^{\bullet})$	
	sp	ap	sp	ap	sp	ap
OH	−0·5	−1·4	−9·7	0·6	−11·6	23·2
O$^-$	−2·4	21·4	1·5^a	2·8^a	−0·4^b	25·4^b
O$^{\bullet}$	9·2	−2·1	—		—	
4-F-BCO		—	6·0^a		24·9^b	
4-Cl-BCO		—	12·2^a		39·9^b	

^{a} Calculated from Eq. (2); ^{b} calculated as $IP(X\text{–}A^-) - IP(A^-)$.
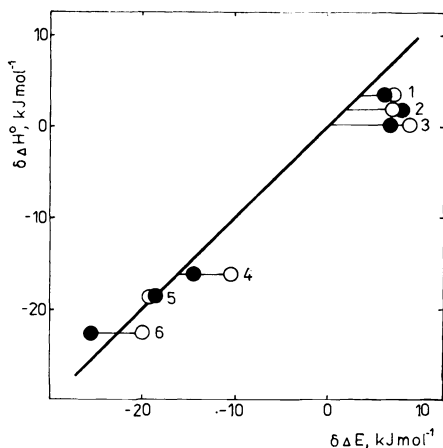

FIG. 1

Test of the electrostatic theory for variable fluoroacids of the general formula F–CH$_2$. .CH$_2$CH$_2$CH$_2$–R. The MNDO $\delta \Delta H^0$ energies are plotted against $\delta \Delta E^0$ ($\circ$) and/or $- \delta \Delta E^0$(EA) ($\bullet$) energies, derived from MNDO geometries. Parent acids (R): **1**, sp COOH; **2**, sp OH; **3**, sp NH$_3^+$; **4**, ap COOH; **5**, ap NH$_3^+$; **6**, ap OH. The straight line has the theoretical slope

a smaller extent to the interactions in the neutral molecules.[18,19] The high difference in the $\delta \Delta H_C^0$ for the sp conformer of I for R = OH $(-0.5 \text{ kJ mol}^{-1})$ vs R = O˙ $(9.2 \text{ kJ mol}^{-1}$, Table V), similarly as for the protonated amines,[8] cannot be explained adequately in terms of the electrostatic theory. A possible reason may be the failure of the MNDO method itself, viz. in an overestimation of the short-range interaction of the C—F dipole in the sp hydroxyl radical.

A perpetual problem is the determination of the magnitude of the substituent effects on homolytic bond dissociation energy $DH^0(\text{A–H})$ during the proton transfer reaction (A). The experimental $\delta \Delta H^0$ and related $\delta \text{EA}(\text{A}^{\cdot})$ data, which might enable one to obtain the $\delta DH^{\circ}(\text{A–H})$ energies, are very limited[13–15,36] and none of them were obtained in the gas phase. This is why we decided to calculate the $\delta DH^0(\text{A–H})$ energies for reaction (D), though only at a MNDO level. The values are given in Tables IV and V. The electron affinities $\delta \text{EA}(\text{A}^{\cdot})$ tally well with the dominant role of the substituent effect in ap conformer of I and 4-X-BCO, whereas the $\delta \text{EA}(\text{A}^{\cdot})$ for sp conformer of I is considerably overestimated $(-11.6 \text{ kJ mol}^{-1}$, Table V). As have been mentioned previously,[8] the reliability of the MNDO method for the calculation of ΔH_f^0 of the radicals may not be sufficient. An alternative approach based on the MNDO calculated IP (i.e., the negative HOMO energies of the anions X—A$^-$) gives more satisfactory results, especially for the sp conformer of I $(-0.4 \text{ kJ mol}^{-1})$.

Scrutinizing the homolytic bond dissociation energies $\delta DH^0(\text{A–H})$ in Table V, it is obvious that these values are mutually related with the $\delta \text{EA}(\text{A}^{\cdot})$ as described above. Except for the apparently overestimated $(-9.7 \text{ kJ mol}^{-1})$ $\delta DH^0(\text{A–H})$ of the sp conformer of I, the remaining values (from 0.6 to 2.8 kJ mol^{-1}) are consistent with the related experimental value for 4-chlorophenol in di-tert-butyl peroxide solution (1.6 kJ mol^{-1}, ref.[15]). Regardless of the small absolute values of $\delta DH^0(\text{A–H})$, the general pattern of F_D effect on reaction (D) is quite reasonable: the higher the polarity of the O—H bond, the higher the $\delta DH^0(\text{A–H})$ energy. Table IV shows this relationship more explicitly in terms of the relative atomic charges δq_H and δq_O, which predict a decrease of electron density on reaction centres of the ap conformer of I and related 4-X-BCO. A similar trend, although controlled simultaneously by the polarizability effect, show both the gas phase[37] ^{1}H NMR and the solution ^{17}O NMR chemical shifts[38] of aliphatic alcohols.

Summarizing the presented evidence, we can state that the homolytic bond dissociation energies $DH^0(\text{A–H})$ in carboxylic acids, protonated amines or alcohols do not necessarily cancel. Their magnitude would become more important if the respective proton transfer reaction were to be transferred from the gas phase into solution.

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