Can O−H Acid be More Acidic Than Its S−H Analog? A G2 Study of Fluoromethanols and Fluoromethanethiols

Peeter Burk* and Ilmar A. Koppel

Institute of Chemical Physics, Tartu University, Jakobi 2, Tartu 51014, Estonia

Alar Rummel and Aleksander Trummal

National Institute of Chemical Physics and Biophysics, Rävala 10, Tallinn 10143, Estonia

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Acidities and homolytic O−H bond dissociation energies of $CH_nF_{3-n}OH$ and $CH_nF_{3-n}SH$ ($n = 0-3$) were calculated at the G2 level of theory. The variation of the geometry of the neutral species and products of heterolytic and homolytic proton abstraction processes, as well as the energetics (gas-phase acidities and homolytic bond dissociation energies of the title compounds), upon successive fluorine substitution has been studied. The results show that the progressive introduction of fluorine atoms into methanol and methanethiol reduces significantly the acidity gap between the representatives of these two series. Therefore, the calculations indicate that the acidities of CF_3OH and CF_3SH are predicted to be rather close: the former compound is expected to be 0.1 kcal/mol more acidic than its SH counterpart. It was concluded that negative (anionic) hyperconjugation and electrostatic effects are mainly responsible for such behavior.

1. Introduction

It is a well-known fact[1] that the acidity of neutral Brønsted acids increases in going down a column of the periodic table, despite the decrease in electronegativity. This behavior is related to the size and polarizability of the species involved. Therefore, methanol is less acidic than methanethiol ($\Delta G_{acid} = 374.0$ kcal/mol[2] and $\Delta G_{acid} = 350.6$ kcal/mol,[2] respectively), and a similar relationship should also be expected to hold for trifluoromethanol and triflouromethanethiol.

Trifluoromethanol has attracted considerable interest in recent years as a product of the atmospheric degradation of hydrofluorocarbons and hydrochlorofluorocarbons which contain a CF_3 group.[3] Among other properties the gas-phase acidity of CF_3OH has also been measured.[4] The reported acidity (ΔG_{acid} = 323 kcal/mol) is higher than earlier estimations (ΔG_{acid} = 340 kcal/mol[5]), and even higher than that of CF_3SH (ΔG_{acid} = 327.8 kcal/mol[6]). Recent ab initio G2 calculations by Notario et al.[7] seem to support the experimental acidity of CF_3OH. In effect this means that CF_3OH should exceed even $(CF_3)_3COH$ in acidity (ΔG_{acid} = 324 kcal/mol[6]).

The high acidity of CF_3OH is especially surprising in view of the fact that the O−H bond in this molecule is reported to be anomalously strong (119 ± 2 kcal/mol[8]), probably even stronger than the corresponding O−H bond in the water molecule. Both experimental and computational results indicate that the CF_3 group strengthens the O−H bond in CF_3OH relative to that in CH_3OH or similar alcohols. The CF_3 group has an apparent β-stabilizing influence in a number of other systems also. For instance, the peroxide linkage in CF_3OOCF_3 has been measured to be 8 kcal/mol stronger than that of typical alkyl peroxides,[9] and the CF_3O−OH bond is calculated to be stabilized by 3.5 kcal/mol relative to that of CH_3O−OH.[10] Similarly, the C−H bond energy in CF_3CH_3 is about 8.5 kcal/mol greater than that in ethane[9] and the C−H bond in $(CF_3)_3CH$ 8.7 kcal/mol stronger than in $(CH_3)_3CH$.[11] At the same time, similar to CF_3OH, $(CF_3)_3CH$ also has a surprisingly high acidity (ΔG_{acid} = 326.6 kcal/mol[6]), which successfully competes with that of $(CF_3)_3OH$ (ΔG_{acid} = 324.0 kcal/mol[6]). While the trend toward the stabilization of β bond energies is evident, the origin of the effect is unclear.

The CF_3 group is well-known to bond strongly to adjacent π-donor groups. This ability has been attributed to the negative hyperconjugation effect, or the ability of the formally π-saturated CF_3 group to act as a π-acceptor.[12,13] Wallington et al. have suggested that the effectiveness of negative hyperconjugation in CF_3OH and CF_3O radical can account for the anomalously large CF_3O−H bond strength.[10,14] On the basis of the simple thermodynamic cycle they showed that the anomalously large value for the CF_3O−H energy can be recast in terms of an anomalously large decrease in C−O bond energy from CF_3OH to CF_3O. As an explanation for this large decrease they have proposed that negative hyperconjugation is less effective in stabilizing the CF_3O radical compared to CF_3OH, and in this way changes in negative hyperconjugation at the C−O bond (α-effect) can be manifested in the hydroxyl bond energies (β-effect).

In the current work, the acidities of $CH_{3-n}F_nOH$ and $CH_{3-n}F_nSH$ ($n = 0-3$) families were calculated at the G2 level of theory. The factors responsible for the behavior of the geometries and energetics of these species and their heterolytic and homolytic dissociation products are discussed.

2. Methodology

Standard ab initio molecular orbital calculations were performed at the G2[15] level using the Gaussian94 program.[16] Geometries of the $CH_{3-n}F_nOH$ and $CH_{3-n}F_nSH$ ($n = 0-3$) molecules and of the corresponding anions and radicals were fully optimized at the HF/6-31G* and MP2/6-31G* levels. Harmonic frequencies were calculated at the HF/6-31G* level of theory.

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TABLE 1: MP2/6-31G* Bond Lengths in $CH_{3-n}F_nOH$ and $CH_{3-n}F_nSH$ ($n = 0-3$) and the Corresponding Anions and Radicals (Å)

	neutral				anion			radical		
	r(C−H)	r(O−H)	r(C−O)	r(C−F)	r(C−H)	r(C−O)	r(C−F)	r(C−H)	r(C−O)	r(C−F)
CH_3OH	1.0897	0.9699	1.4234		1.1486	1.3232		1.1008	1.3861	
	1.0969							1.0959		
	1.0969							1.0959		
CH_2FOH	1.0891	0.9724	1.3839	1.3900	1.1310	1.2684	1.5586	1.0999	1.3406	1.3841
	1.0954							1.0999		
CHF_2OH	1.0873	0.9756	1.3579	1.3659	1.1165	1.2386	1.4791	1.0983	1.3520	1.3567
CF_3OH		0.9739	1.3499	1.3304		1.2257	1.4311		1.3662	1.3362
				1.3506						1.3368
				1.3506						1.3368

	neutral				anion			radical		
	r(C−H)	r(O−H)	r(C−O)	r(C−F)	r(C−H)	r(C−O)	r(C−F)	r(C−H)	r(C−O)	r(C−F)
CH_3SH	1.0899	1.3398	1.8138		1.0995	1.8256		1.0947	1.7992	
	1.0897							1.0901		
	1.0897							1.0901		
CH_2FSH	1.0913	1.3402	1.7958	1.3887	1.0993	1.7713	1.4436	1.0948	1.7762	1.3632
	1.0907							1.0948		
CHF_2SH	1.0909	1.3408	1.7947	1.3645	1.0976	1.7391	1.4126	1.0944	1.7935	1.3632
CF_3SH		1.3401	1.7968	1.3427		1.7275	1.3883		1.8008	1.3459
				1.3460						1.3433
				1.3460						1.3433

Deprotonation energies (DPE) were calculated as the energies of the reaction

$$HA \rightleftharpoons A^- + H^+$$

using G2 energies at 0 K ($E(H^+)_{0K} = 0.0$):

$$DPE = E(A^-) + E(H^+) - E(HA)$$

ΔH_{acid} and ΔG_{acid} were calculated (at 298 K) similarily using thermochemical corrections from frequency calculations[17] (taking into account the proper symmetry) for comparison with experiment. Homolytic bond dissociation energies (BDE) were calculated as the energies of the reaction

$$HA \rightleftharpoons A^* + H^*$$

$$BDE = E(AH) - [E(A^*) + E(H^*)]$$

and ΔH_{HBD} and ΔG_{HBD} were also calculated (at 298 K).

3. Results and Discusson

3.1. Geometries. In Table 1 are listed the geometries of investigated methanols and methanethiols optimized at the MP2/6-31G* level of theory. Both monofluorinated methanol and methanethiol adopted conformations with OH or SH hydrogen gauche to the fluoro substituent (Figures 1 and 2). The trans conformer was not a minimum on the MP2/6-31G* CH_2FOH potential energy surface but rather a transition state (5.5 kcal/mol above the minimum) by analogy with fluoromethylamine.[18] Interestingly enough the cis (staggerred) conformation of CH_2FOH, which is also a transition state to the rotation around O−H bond, has lower energy (3.0 kcal/mol above the minimum energy gauche form). In the case of CH_2FSH the two corresponding transition states have much closer energies (4.0 and 3.8 kcal/mol above the minimum for trans and staggered conformations, respectively).

In difluoro-substituted acids the OH and SH hydrogens were also oriented gauche relative to both fluoro substituents (Figures 1 and 2). The gauche−trans conformers were local minima on the potential energy surface, but above (by 3.1 kcal/mol for CHF_2OH and 1.1 kcal/mol for CHF_2SH) the global gauche−gauche minima, and the energy barrier for conversion of the trans−gauche conformer into the gauche−gauche conformer was found to be small or even negligible (0.1 and 1.3 kcal/mol for CHF_2OH and CHF_2SH, respectively).

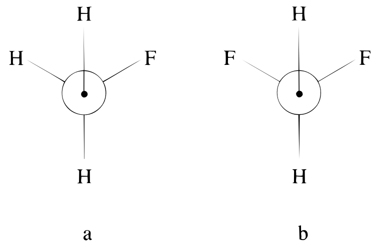

Figure 1. Preferred conformations of (a) CH_2FOH and CH_2FSH and (b) CHF_2OH and CHF_2SH.

Such conformational preferences have been observed earlier for substituted methanols[14] and attributed to the hyperconjugative interaction between fluoro substituents and lone pairs of the hydroxyl oxygen. Another possible explanation would attribute such behavior to the electrostatic interaction: the O−H (and also S−H) bond dipoles are oriented opposite those of the CH_2F and CHF_2 groups, similarly to the orientation of O−H groups in carboxylic acids preferably as *Z* (over *E*).[18] It is clear that electrostatics should be much less important for S−H compounds as the S−H bond dipole moment is much smaller than that of the O−H bond (due to the smaller electronegativity difference). The distinct differences between potential energy curves for CH_2FOH and CH_2FSH, and CHF_2OH and CHF_2SH—especially the marked stabilization of the staggered transition state (maximum of the electrostatic stabilization—antiparallel dipole moments) relative to the trans form (maximum of electrostatic destabilization—parallel dipole moments) in the case of CH_2FOH and the absence of a similar effect in the case of CH_2FSH—indicate that the electrostatic interactions are operative.

Geometries, calculated at the MP2/6-31G* level (see Table 1), indicate that successive fluorine substitution does not affect C−H, O−H, and S−H bond lengths to a considerable extent. The largest geometric changes take place in the C−O and C−F bond lengths in neutral methanols. Upon fluorination the C−O bond in neutral substituted methanols is shortened by 0.040,

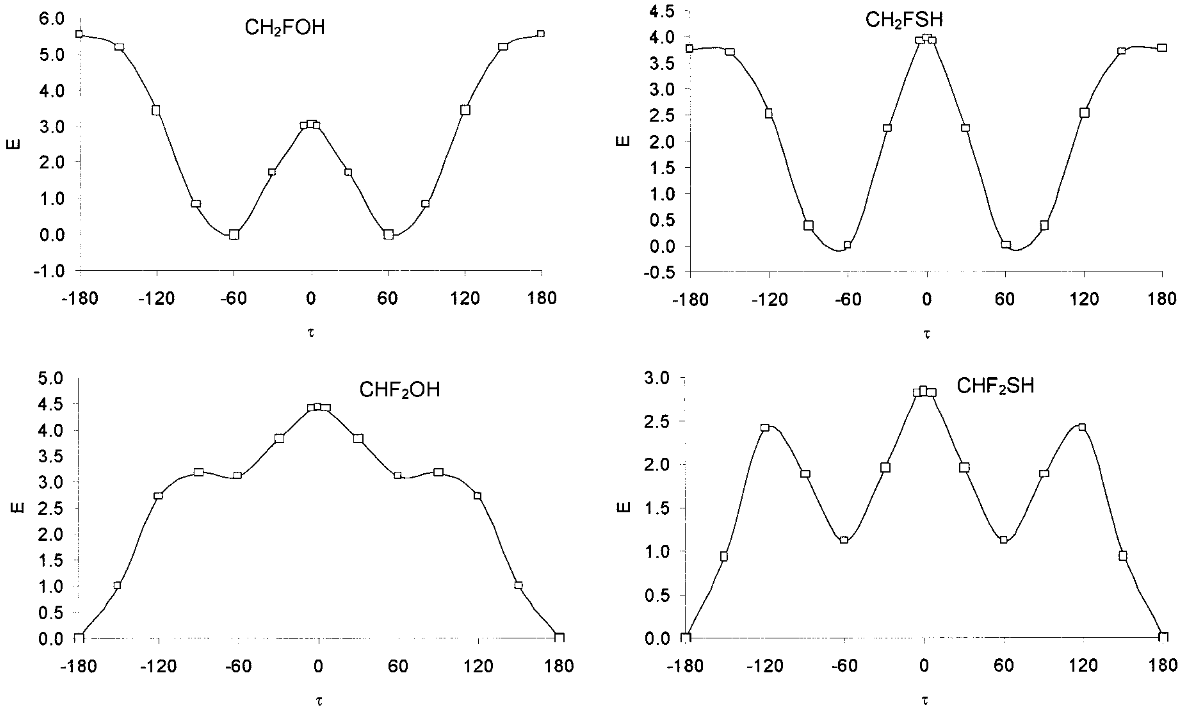

Figure 2. Energy barriers for rotations around the C−O and C−S bonds in CH_2FOH, CH_2FSH, CHF_2OH, and CHF_2SH. Energies *E* are relative to the preferred conformation (kcal/mol). τ is the dihedral angle H−O−C−F for CH_2FOH, H−S−C−F for CH_2FSH, H−O−C−H for CHF_2OH, and H−S−C−H for CHF_2SH.

0.026, and 0.008 Å, while C−F bond is shortened by 0.024 and 0.015 Å. The C−S bond in methanethiols is shortened by 0.018 Å upon the first fluorine inclusion and remains practically constant upon successive fluorination, thus behaving similarly to the C−H bonds in methanol. These trends are similar to those well-known in the CF_xH_{4-x} series, first noted by Brockway.[19] They have usually been taken as evidence for negative hyperconjugation in CF_xH_{4-x},[20] but Wiberg[21] and Reed and Schleyer[20] have attributed them to the Coulombic interaction.

In the series of substituted methoxide anions the C−H and especially C−F bonds are longer than their counterparts in neutrals (by 0.03−0.06 and 0.1−0.12 Å, respectively), while the C−O bond is shorter by 0.1−0.12 Å. Successive fluorination leads to the C−H bond being shortened by 0.017 and 0.014 Å, while C−F bonds are lengthened by 0.079 and 0.048 Å. Similarly, the C−H and C−F bonds are longer (compared to those in neutrals) in substituted metylthio anions and the C−S bonds shorter by 0.02−0.07 Å, except for that in CH_3S^-, where the C−S bond is 0.012 Å longer than in the neutral. Here the successive fluorination also has the C−H and C−F bond shortening effect, but the changes are smaller (0.0002 and 0.0017 Å for C−H bonds and 0.031 and 0.024 Å for C−F bonds). In contrast, the changes in C−S bond lengths are much more pronounced for anions compared to neutrals, and are 0.054, 0.032, and 0.012 Å.

The C−H bonds gauche to the orbital with an unpaired electron are somewhat shorter in methoxy and methylthio radicals compared to methanol and methanethiol, while the trans C−H bond is longer compared to the similar bonds (relative to the O−H bond) in methanol and methanethiol. Substitution of hydrogens by fluorines has a very small effect (up to 0.0025 Å for methanols and 0.0047 Å for methanethiols) on C−H bonds. The C−O bond is much shorter in methoxy radical compared to methanol (by 0.038 Å), but still longer than in methoxy anion, while the C−S bond in methylthio radical is 0.015 and 0.026 Å shorter than in methanethiol and methylthio anion, respectively. In all radicals the subsequent inclusion of fluorines leads to the shortening of C−F bonds (by 0.028 and 0.020 Å for methoxy radicals and by 0.024 and 0.020 Å for methylthio radicals). Inclusion of the first fluorine into methoxy and methylthio radicals leads to the marked decrease of the C−O and C−S bonds as in the case of neutrals and anions. In contrast, the inclusion of the second and third fluorine leads to the lengthening of the corresponding C−O and C−S bonds.

TABLE 2: G2 Energies (*E*, au), Deprotonation Energies (DPE, kcal/mol), and Homolytic Bond Dissociation Energies (BDE, kcal/mol) at 0 K for the Studied O−H and S−H Acids

	E(AH)	*E*(A^-)	*E*(A*)	DPE	BDE
H_2O	−76.332 06	−75.712 78	−75.643 91	388.6	118.1
FOH	−175.353 41	−174.781 03	−174.696 27	359.2	98.6
CH_3OH	−115.534 90	−114.927 09	−114.867 53	381.4	105.0
CH_2FOH	−214.702 00	−214.132 25	−214.034 80	357.5	104.9
CHF_2OH	−313.879 04	−313.336 90	−313.195 17	340.2	115.4
CF_3OH	−413.051 70	−412.530 52	−412.362 57	327.0	118.7
H_2S	−398.930 71	−398.371 58	−398.286 97	350.9	90.2
FSH	−498.050 20	−497.503 70	−497.418 20	342.9	82.8
CH_3SH	−438.148 47	−437.579 77	−437.511 26	356.9	86.1
CH_2FSH	−537.300 52	−536.750 71	−536.663 08	345.0	86.3
CHF_2SH	−636.464 12	−635.932 07	−635.821 35	333.9	89.6
CF_3SH	−735.635 44	−735.115 73	−734.991 83	326.1	90.1

3.2. Energetics. G2 energies, deprotonation energies, and homolytic bond dissociation energies (at 0 K) are given in Table 2. G2 enthalphies, Gibbs energies, acidities, and homolytic bond dissociation enthalpies and Gibbs energies (all at 298.15 K) are given in Tables 3 and 4 along with experimental gas-phase acidities. In most cases where comparisons are available, the experimental and calculated acidities are in reasonable agreement (usually within ±2 kcal/mol) with each other.

However, more noticeable deviation is present in case of CF_3-SH, where the difference between the available experimental acidity value and G2 calculations amounts to more than 6 kcal/mol. Unfortunately, the performance of the G2 theory for reproducing the gas-phase acidities was never checked for

TABLE 3: G2 Gibbs Energies (G, au), Gas-Phase Acidities (ΔG_{acid}, kcal/mol), and Homolytic Bond Dissociation Gibbs Energies (ΔG_{homol}, in kcal/mol) for the Studied O−H and S−H Acids at 298.15 K, and the Corresponding Experimental Gas-Phase Acidities (ΔG_{acid}^{exptl}, kcal/mol)

	G(AH)	G(A$^-$)	G(A*)	ΔG_{acid}	ΔG_{acid}^{exptl}	ΔG_{homol}
H_2O	−76.349 65	−75.729 03	−75.660 80	383.4	384.1[27]	111.2
FOH	−175.375 19	−174.801 24	−174.716 90	354.1	355.6[28]	92.1
CH_3OH	−115.557 62	−114.948 25	−114.890 46	376.3	374.0[2]	97.6
CH_2FOH	−214.726 74	−214.156 77	−214.059 87	351.6		97.4
CHF_2OH	−313.905 36	−313.363 01	−313.221 86	334.2		107.9
CF_3OH	−413.079 22	−412.556 66	−412.390 60	320.9	323.0[4]	111.1
H_2S	−398.950 22	−398.389 43	−398.305 45	345.8	344.8[2]	83.6
FSH	−498.073 43	−497.525 02	−497.440 02	338.0		76.4
CH_3SH	−438.172 69	−437.602 33	−437.535 54	351.8	350.6[2]	78.8
CH_2FSH	−537.326 65	−536.776 41	−536.689 39	339.2		78.9
CHF_2SH	−636.491 83	−635.959 27	−635.849 26	328.1		82.2
CF_3SH	−735.664 17	−735.142 89	−735.021 00	321.0	327.8[6]	82.6

TABLE 4: G2 Enthalpies (H, au), Gas-Phase Acidities (ΔH_{acid}, kcal/mol), and Homolytic Bond Dissociation Enthalpies (ΔH_{homol}, kcal/mol) for the Studied O−H and S−H Acids at 298.15 K, and the Corresponding Experimental Gas-Phase Acidities (ΔH_{acid}^{exptl}, kcal/mol)

	H(AH)	H(A$^-$)	H(A*)	ΔH_{acid}	ΔH_{acid}^{exptl}	ΔH_{homol}
H_2O	−76.328 28	−75.709 47	−75.640 60	389.8	390.7[27]	119.3
FOH	−175.349 59	−174.777 63	−174.692 93	360.4	362.5[28]	99.8
CH_3OH	−115.530 61	−114.923 24	−114.863 56	382.6	380.6[2]	106.3
CH_2FOH	−214.697 54	−214.128 04	−214.030 69	358.8		106.2
CHF_2OH	−313.874 18	−313.332 33	−313.190 67	341.5		116.6
CF_3OH	−413.046 27	−412.525 51	−412.3573 82	328.3	329.8[4]	120.0
H_2S	−398.926 91	−398.368 28	−398.283 67	352.0	350.7[2]	91.4
FSH	−498.046 31	−497.500 27	−497.414 82	344.1		84.0
CH_3SH	−438.143 89	−437.575 75	−437.507 10	358.0	357.6[2]	87.3
CH_2FSH	−537.295 64	−536.746 35	−536.658 72	346.2		87.4
CHF_2SH	−636.458 68	−635.927 25	−635.816 44	335.0		90.7
CF_3SH	−735.629 44	−735.110 35	−734.986 22	327.2		91.4

relatively more acidic Brönsted acids, and a question of whether any scaling of the directly calculated ΔG_{acid} values is neccessary remains unanswered. Therefore, on those grounds it is probably too early to call for the urgent revision of the published experimental value for CF_3SH. Our experience[22] with G2 calculations of intrinsic acidities of some strong conventional acids (e.g., FSO_3H) seems to support the necessity of such scaling.

At the same time, it is evident that the two most acidic representatives of the series of fluorine-substituted methanols and methanethiols, respectively, CF_3OH and CF_3SH, are predicted by G2 theory to have rather close intrinsic acidity. Indeed, in sharp contrast to, e.g., methanol and methanethiol (the latter is 23.4 kcal/mol more acidic than CH_3OH) or water and H_2S (the latter is 39.3 kcal/mol more acidic than H_2O), trifluoromethanol exceeds CF_3SH in calculated gas-phase acidity by 0.1 kcal/mol at 298 K! It should be noted that at 0 K the CF_3SH is still predicted to be a stronger acid by 0.8 kcal/mol, and the inversion of the acidity order is due to an entropy factor: on the ΔH_{acid} scale (at 298 K) CF_3SH is by 1.1 kcal/mol a stronger acid compared to CF_3OH.

At the same time, the calculated gas-phase acidities for both CF_3OH and CF_3SH also exceed the experimentally determined ΔG_{acid} value for $(CF_3)_3COH$ (324.0 kcal/mol), whereas the G2 calculated acidity for the latter is not available due the computational problems connected to its size.

There is no doubt that CF_3OH and CF_3SH play an important role in understanding the influence of substituent effects on the acidity of fluorine-substituted alcohols and thiols. However, the procedures of measurement of their gas-phase acidity are rather complicated, in particular because of the presence of different competing side reactions which are most pronounced in the case of CF_3OH (elimination of HF, formation of H-bonded complexes with F$^-$, etc.). Therefore, an additional careful study, review and verification of the experimental data on the gas-phase acidities of both CF_3OH and CF_3SH, seems to be highly desirable.

Inspection of the acidity trends shows (as expected) increased acidity after each successive fluorine introduction. Also, quite logically, each additional replacement of hydrogen by fluorine leads to a smaller acidity increase compared to those of the previous ones. Interestingly, in the case of methanethiol, the acidifing effects ($\Delta\Delta G_{acid}$) of the first and second fluorine substitutions are quite close (12.6 and 11.1 kcal/mol), while the third substitution leads to much smaller acidity enhancement (7.1 kcal/mol). The successive fluorine substitutions in methanol lead to a much smoother acidity increase: 24.7, 17.4, and 12.4 kcal/mol, respectively. Therefore, in the case of the series of substituted methanols, the effects are much larger than in methanethiol.

Changes in homolytic bond dissociation energies ($\Delta\Delta H_{HBD}$) are much more confusing. In both series of substituted methanols and methanethiols, the first fluorine substitution practically does not change the bond dissociation energy, while the second substitution leads to the marked increase of the BDE (10.4 kcal/mol in the case of methanol and 3.3 kcal/mol for methanethiol). The third substitution has very a small effect on the BDE of methanethiol (0.4 kcal/mol). In the case of methanol the effect is 3.4 kcal/mol, which is also considerably smaller than the effect of the second substitution. From these data it is clear that the effect responsible for the BDE increase is not a simple inductive effect as suggested for fluorinated ethanols,[11] where the monotonous (although not quite linear) increase in the BDE with successive replacemens of β-hydrogens by fluorine atoms was found.

Figure 3 presents the relationships between the acidities of investigated O−H and S−H acids, and between homolytic bond dissociation energies of the same compounds. One can see that

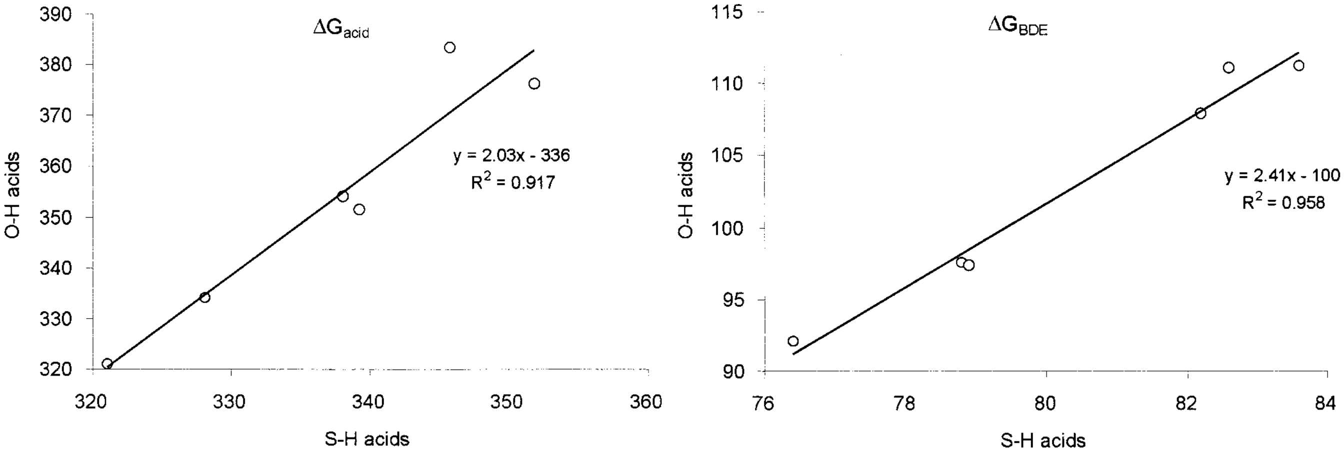

Figure 3. Correlation between calculated acidities (at 298 K) of O−H and S−H acids, and between calculated homolytic bond dissociation free energies (at 298 K) of O−H and S−H acids.

the structural effects on the acidities and BDEs of both families are linearly related to a high degree of precision ($R^2 = 0.917$ and $R^2 = 0.958$, respectively), while the slopes of correlation lines are significantly larger than 1 (in fact 2.03 and 2.41, respectively). Thus, in accord with the earlier work of Molina et al.,[23] substituent effects are appreciably attenuated in thiols with respect to alcohols, possibly as a consequence of the S−C bonds being longer than the O−C ones.

Wallington has proposed hyperconjugation as the explanation of BDE trends in fluoromethanols. He argues that a single fluorine substituent can have a hyperconjugative interaction only with one free electron pair on oxygen, thus stabilizing both CH_2FOH and CH_2FOH radicals to the same extent (as both species have an oxygen lone pair available). In contrast, he writes[14] "Multiple halogen substituents can interact with and stabilize two O π-electron pairs on an adjacent oxygen. Approximately two electron pairs are available in the saturated methanols, but in the methoxy radicals only one pair plus one unpaired electron are available."

Besides the interactions between fluorine substituents and oxygen, one should also consider the interactions between fluorine atoms in multiply substituted species as it is well known that carbon energetically prefers to be multiply substituted by fluorine.[21] The extra stability of multiply substituted fluoromethanes as compared to the methyl fluoride has also been commonly discussed in terms of negative hyperconjugation. However, Wiberg has proposed[21] that this phenomenon can also be explained on the grounds of simple electrostatic interactions.

The energetic effects of subsequent fluorination can be compared using the energies of the following isodesmic reaction:

$$CH_nF_{3-n}X + CH_3F \rightleftharpoons CH_{n-1}F_{4-n}X + CH_4$$

where X is OH, SH, O^-, S^-, $O^\bullet$, or $S^\bullet$. Table 5 shows that for substituted methanols the inclusion of the second and third fluorine atoms leads to higher stabilization of the molecule as compared to the first fluorine substituent, whereas the second fluorine is the most stabilizing. Interestingly enough, the stabilization energies obtained by stepwise introduction of fluorines into methanol (14.9, 21.1, and 18.4 kcal/mol) are very close to those obtained from the isodesmic reaction

$$CH_nF_{4-n} + CH_3F \rightleftharpoons CH_{n-1}F_{5-n}X + CH_4$$

($1 \le n \le 3$) for introduction of fluorines into methane (12.8, 20.2, and 18.4 kcal/mol, based on G2(0 K) energies in Table 6). As we have similar systems here, and the energy trends are also the same, we expect that the stabilizing mechanism should also be the same for both systems.

TABLE 5: Energetics ($E_{(1)}$, kcal/mol) of Stepwise Fluorination by the Isodesmic Reaction $CH_nF_{3-n}X + CH_3F \rightleftharpoons CH_{n-1}F_{4-n}X + CH_4$

molecule	$E_{(1)}^{\text{neutral}}$	$E_{(1)}^{\text{anion}}$	$E_{(1)}^{\text{radical}}$
H_2O	76.6	47.1	57.1
CH_3OH	−14.9	−38.8	−15.0
CH_2FOH	−21.1	−38.5	−10.7
CHF_2OH	−18.4	−31.5	−15.1
H_2S	15.0	7.1	7.6
CH_3SH	−5.5	−17.3	−5.3
CH_2FSH	−12.7	−23.9	−9.4
CHF_2SH	−17.6	−25.3	−17.0
CH_4	0.0		
CH_3F	−12.8		
CH_2F_2	−20.2		
CHF_3	−18.4		

TABLE 6: G2 Energies (E, au) at 0 K for Methane and Fluoromethanes

	E		E
CH_4	−40.41086	CHF_3	−337.89358
CH_3F	−139.55422	CF_4	−437.06631
CH_2F_2	−238.71798		

In case of substituted methoxy anions the stabilizing energies of fluorine substitution are the largest (up to 38.8 kcal/mol for the first fluorine), and decrease somewhat as the degree of fluorination increases. For methoxy radical the first and third substitutions are energetically practically identical (15.0 and 15.1 kcal/mol, respectively), while the second one is somewhat smaller (10.7 kcal/mol). These energy trends in methoxy radicals contradict the electrostatic model proposed by Wiberg[21] as there should not be any reason for lesser electrostatic stabilization in difluoromethoxy radical compared to trifluoromethoxy radical neither by saturation nor by repulsion between lone pairs of fluorine atoms.

In contrast to substituted methanols, for methanethiol the successive fluorine substitutions stabilize neutrals, anions, and radicals in a synergistic manner, i.e., each successive substitution has more significant stabilization energy. The stabilization energies are greatest for anions as in the case of substituted methanols. The radicals are somewhat less stabilized than neutrals.

Comparison of acidifing effects of fluorine substitution into parent molecules of H_2O and H_2S indicates that the substitution of hydrogen for fluorine has a significantly larger acidifying effect (30 kcal/mol) in the case of a water molecule, whereas in the case of dihydrogen sulfide the acidity increase is only 8 kcal/mol. Assuming the same electronegativity effect in both species and a less significant lone pair−lone pair repulsion effect in FS^- as compared with FO^- this order is hard to understand.[24]

As indicated above, the major structural effects responsible for the rather high acidity of CF_3OH, CF_3SH, and evidently also $(CF_3)_3CH$ are negative (anionic) hyperconjugation and electrostatic effects. In the case of those species the first effect seems to be dominating.

However, the conditions could be created, e.g., by introduction of the full positive charge into the alcohol molecule, where the electrostatic effects are by far more responsible for the sharp increase of the acidity of the acid: our calculations using the DFT B3LYP approach at the 6-311+G** level show that the acidity of the protonated form of trimethylamine oxide, $(CH_3)_3$-NOH^+ ($\Delta G_{acid} = 227.5$ kcal/mol[25]), is predicted to be ca. 93 kcal/mol higher than the same quantity for CF_3OH!

4. Summary

Our G2 calculations indicate that the successive introduction of fluorine atoms into methanol and methanethiol significantly reduces the acidity gap between the representatives of those two series. The G2 calculations predict that the ca. 25 kcal/mol stronger acidity of CH_3SH as compared with CH_3OH is inverted to a −0.1 kcal/mol acidity difference (at 298 K) in the case of the respective trifluoromethyl derivatives. Noteworthy, CF_3SH is still marginally stronger than CF_3OH at 0 K and also on the ΔH_{acid} scale (at 298 K).

The energetic effects upon successive fluorination of neutrals, anions, and radicals of investigated species indicate that hyperconjugation is the main effect in charge. The same conclusion can be obtained from geometries, especially from the changes of the C−O and C−S bond lengths upon the inclusion of the second and third fluorine atoms. However, the potential energy curves for rotation around the O−H and S−H bonds suggest that the direct electrostatic interactions (i.e., between bond dipoles) should also be taken into account.

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