Bond Strength Trends in Halogenated Methanols: Evidence for Negative Hyperconjugation?

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Abstract: The hydroxyl bond energies in the series of fluorinated and chlorinated methanols $CF_xH_{3-x}OH$ and $CCl_xH_{3-x}OH$ have been examined using ab initio molecular orbital theory. The O–H bond strength is found to increase with the degree of halogenation, with fluorine substituents having a greater effect than chlorine substituents. The bond strengthening is not, however, directly related to the degree of halogenation. Rather, the bond energy appears to increase in a manner that coincides with the effectiveness of negative hyperconjugation between the methyl and hydroxyl groups. The trends are consistent with the notion that bond strengthening arises from a decrease in effectiveness of negative hyperconjugation from the methanol to the methoxy radical, the difference being manifested in a modification of the O–H bond strength. Support for this model is provided by the calculated bond length trends, conformational preferences, radical state energy separations, and orbital populations.

Introduction

The hydroxyl bond energy in CF_3OH is of current interest because of its relevance to the atmospheric oxidation of hydrofluorocarbons (HFCs). The CF_3O radical may be produced during the atmospheric degradation of a variety of HFCs, including HFC-23 (CF_3H),[1] HFC-125 (CF_3CF_2H),[2-4] HFC-134a (CF_3CFH_2),[5,6] and HFC-143a (CF_3CH_3).[7] An important atmospheric fate of CF_3O radicals is reaction with hydrogen donors such as alkanes:[8]

$$CF_3O + RH \rightarrow CF_3OH + R \qquad (1)$$

The reaction of CF_3O radicals with a variety of alkanes has been investigated experimentally.[9-14] In all the cases studied, the kinetics of reaction 1 are found to be similar to the analogous alkane plus hydroxyl radical reactions, suggesting a corresponding similarity in CF_3O–H and HO–H bond strengths. Congruent with these observations, evidence has also been presented that CF_3O radicals react slowly with water ($k_2 = 0.02$ to 4×10^{-16} cm^3 molecule^{-1} s^{-1}):[15]

$$CF_3O + H_2O \rightarrow CF_3OH + OH \qquad (2)$$

These kinetic results also suggest that the CF_3O–H bond strength is at least comparable to the O–H bond strength in water.

The experimental evidence for an unusually large hydroxyl bond strength in CF_3OH is supported by theoretical considerations. This system was first studied by Batt and Walsh, who used a combination of experimental data and bond additivity arguments to predict a CF_3O–H bond energy of 109 kcal mol^{-1},[16] compared to a typical unsubstituted alkyl alcohol O–H bond strength of 103 to 105 kcal mol^{-1}.[17] Francisco used a direct ab initio approach to predict a CF_3O–H bond energy of about 101 kcal mol^{-1},[18] but more recent ab initio work from our[19] and other[20] laboratories indicates that the value is likely much larger. The best currently available computed value is 119 ± 2 kcal mol^{-1}, again comparable to that of the O–H bond in water.[19]

The 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 peroxy linkage in CF_3OOCF_3 has been measured to be 8 kcal mol^{-1} stronger than that of typical alkyl peroxides,[17,21] and the CF_3O–OH bond is calculated to be stabilized by 3.5 kcal mol^{-1} relative to CH_3O–OH.[19] Similarly, the C–H bond energy in CF_3CH_3 is about 8.5 kcal mol^{-1} greater than that in ethane.[17] While the trend toward stabilization of β bond energies is evident, the origin of the effect is unclear.

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Table 1. RHF/6-31G(d,p) Optimized Geometries[a]

	CH_3OH $X_1 = X_2 = H$	CFH_2OH[b] $X_1 = F, X_2 = H$	CF_2HOH $X_1 = H, X_2 = F$	CF_3OH $X_1 = X_2 = F$	$CClH_2OH$[b] $X_1 = Cl, X_2 = H$	CCl_2HOH $X_1 = H, X_2 = Cl$	CCl_3OH $X_1 = X_2 = Cl$
$r(C-O)$	1.3984	1.3631	1.3387	1.3297	1.3631	1.3458	1.3441
$r(O-H)$	0.9422	0.9443	0.9470	0.9458	0.9444	0.9466	0.9476
$r(C-X_1)$	1.0820	1.3616	1.0758	1.3047	1.8084	1.0726	1.7586
$r(C-X_2)$	1.0883	1.0792 1.0848	1.3372	1.3205	1.0756 1.0802	1.7856	1.7844
$\angle(H-O-C)$	109.62	110.14	110.05	110.53	110.59	111.14	110.44
$\angle(O-C-X_1)$	107.34	110.72	109.60	108.91	112.32	108.69	107.19
$\angle(O-C-X_2)$	112.14	107.58 112.46	110.96	111.91	108.28 113.46	111.93	110.79
$\angle(X_1-C-O-H)$[c]	180.00	64.24	180.00	180.00	65.19	180.00	180.00
$\angle(X_1-C-O-X_2)$[d]	118.78	118.28 119.41	121.26	120.12	117.14 119.31	118.30	119.87

[a] Distances in angstroms and angles in degrees. X_1 is the symmetry-unique substituent (H, F, or Cl) under C_s symmetry; X_2 are the two symmetry-equivalent substituents. [b] C_1 symmetry. [c] Dihedral angle between X_1CO and COH planes. [d] Dihedral angle between X_1CO and X_2CO planes.

Table 2. UHF/6-31G(d,p) Optimized Geometries[a]

	CH_3O $X_1 = X_2 = H$	CFH_2O $X_1 = F, X_2 = H$	CF_2HO $X_1 = H, X_2 = F$	CF_3O $X_1 = X_2 = F$	$CClH_2O$ $X_1 = Cl, X_2 = H$	CCl_2HO $X_1 = H, X_2 = Cl$	CCl_3O $X_1 = X_2 = Cl$
$r(C-O)$	1.3824	1.3443	1.3464	1.3527	1.3490	1.3459	1.3510
$r(C-X_1)$[b]	1.0885	1.3541	1.0828	1.3067	1.7957	1.0808	1.7712
$r(C-X_2)$[b]	1.0862	1.0855	1.3273	1.3084	1.0818	1.7735	1.7661
$\angle(O-C-X_1)$	106.16	112.57	106.85	106.70	113.79	106.11	111.87
$\angle(O-C-X_2)$	111.69	108.37	111.10	111.36	109.13	111.82	106.60
$\angle(X_1-C-O-X_2)$[c]	117.89	119.94	120.44	119.74	119.71	117.52	120.29

[a] Distances in angstroms and angles in degrees. [b] X_1 is the symmetry-unique substituent (H, F, or Cl) under C_s symmetry; X_2 are the two symmetry-equivalent substituents. [c] Dihedral angle between X_1CO and X_2CO planes.

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.[22,23] We have previously suggested that differences in the effectiveness of negative hyperconjugation in CF_3OH and CF_3O radical can account for the anomalously large CF_3O-H bond strength.[19] From simple thermochemical considerations, for any alcohol ROH the difference in C−O bond energies R−OH and R−O is, to within an additive constant, equal to the hydroxyl bond energy RO−H:

$$DH°(RO-H) = DH°(R-OH) - DH°(R-O) + DH°(O-H) \quad (3)$$

where DH°(O−H) is the bond energy of the hydroxyl radical. In the simple alkyl alcohols (e.g. CH_3OH) the difference DH°(R−OH) − DH°(R−O) is invariably about 4 kcal mol^{-1}, so that the alcohol bond strengths are essentially constant. In CF_3OH, however, the difference is far larger (about 17 kcal mol^{-1}),[19] resulting in a concomitant increase in the CF_3O-H bond strength. Thus, the anomalously large value for DH°(CF_3O-H) can be recast in terms of an anomalously large decrease in C−O bond energy from CF_3OH to CF_3O. One possible explanation for this large decrease is that negative hyperconjugation is less effective in stabilizing the CF_3O radical compared to CF_3OH. In this way, changes in negative hyperconjugation at the C−O bond (α effect) can be manifested in the hydroxyl bond energies (β effect).

To explore this model further, we have extended the earlier ab initio calculations on CF_3OH to the complete series of fluorinated and chlorinated methanols and methoxy radicals $CF_xH_{3-x}O(H)$ and $CCl_xH_{3-x}O(H)$. The O−H and C−O bond strengths in these series have been determined from isodesmic reactions evaluated at the MP2/6-31G(d,p) level. These substituted methanols have all been observed experimentally,[24,25] although in no case besides CF_3OH is experimental information pertaining to the O−H bond strength available. The computational results indicate that the O−H and C−O bond energies do increase with the degree of halogenation, with fluorine substituents having a greater effect than chlorine. However, the increase is not a linear function of the degree of substitution. Rather, the increase follows a pattern consistent with the role of negative hyperconjugation outlined above and its anticipated dependence on the structural details of the species involved. Further evidence for the importance of negative hyperconjugation is provided by the calculated conformational preferences, bond length trends, radical state orderings, and orbital populations.

In this report we attempt to predict and analyze the trends among these related compounds. The methods we employ are expected to provide qualitatively correct geometric and energetic information. The results compare favorably with the limited number of available higher-level calculations and lend support to the notion that negative hyperconjugation effects can be manifested in bonds removed from the center of conjugation.

Computational Details

All calculations were performed using the Gaussian 88 program.[26] All molecules were gradient-optimized[27,28] at the Hartree−Fock level (restricted for closed-shell molecules, unrestricted otherwise) using

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Table 3. Calculated Electronic and Thermal Energies[a]

	state	(U)HF	(U)MP2	ZPE	ΔE^{298}	total[b]
CH_3	$^2A_2''$	−39.564 46	−39.692 70	0.027 76	0.003 21	−39.533 48
CH_3O	$^2A'$	−114.425 58	−114.709 70	0.035 95	0.002 96	−114.670 79
CH_3OH	$^1A'$	−115.046 71	−115.381 11	0.409 62	0.003 27	−115.328 23
CFH_2	$^2A'$	−138.402 11	−138.695 12	0.024 21	0.002 92	−138.667 99
CFH_2O	$^2A''$	−213.285 50	−213.729 76	0.030 70	0.003 08	−213.695 98
CFH_2OH[c]	^1A	−213.909 08	−214.402 31	0.044 04	0.003 39	−214.354 88
CF_2H	$^2A'$	−237.265 19	−237.715 43	0.018 82	0.003 05	−237.693 56
CF_2HO	$^2A'$	−312.147 08	−312.748 89	0.024 25	0.003 40	−312.721 24
CF_2HOH	$^1A'$	−312.783 99	−313.436 63	0.036 96	0.003 73	−313.395 94
CF_3	$^2A_1$	−336.131 18	−336.741 64	0.012 20	0.003 33	−336.726 10
CF_3O	$^2A'$	−411.013 25	−411.774 37	0.016 41	0.004 02	−411.753 95
CF_3OH	$^1A'$	−411.654 85	−412.466 41	0.028 90	0.004 23	−412.433 28
$CClH_2$	$^2A'$	−498.464 72	−498.713 62	0.022 08	0.003 17	−498.688 37
$CClH_2O$	$^2A''$	−573.328 28	−573.733 99	0.028 86	0.003 30	−573.701 83
$CClH_2OH$[c]	^1A	−573.953 19	−574.408 24	0.042 33	0.003 58	−574.362 33
CCl_2H	$^2A'$	−957.359 82	−957.733 37	0.015 28	0.003 51	−957.714 58
CCl_2HO	$^2A'$	−1 032.215 43	−1 032.746 82	0.020 44	0.004 03	−1 032.722 35
CCl_2HOH	$^1A'$	−1 032.847 79	−1 033.429 14	0.033 49	0.004 25	−1 033.391 40
CCl_3	$^2A_1$	−1 416.248 16	−1 416.749 15	0.007 15	0.004 31	−1 416.737 79
CCl_3O	$^2A'$	−1 491.094 43	−1 491.756 86	0.010 81	0.005 09	−1 491.740 97
CCl_3OH	$^1A'$	−1 491.726 89	−1 492.438 47	0.023 41	0.005 25	−1 492.409 82

[a] All energies in au. [b] MP2/6-31G(d,p) energy + ZPE + ΔE^{298}. [c] C_1 symmetry.

Pople's split-valence 6-31G(d,p) basis set.[29] Harmonic vibrational modes were evaluated analytically. The structural parameters for the methanol and methoxy species are included in Tables 1 and 2, respectively. The series of methoxy radicals were all assumed to possess C_s symmetry. In each case, both the $^2A'$ and $^2A''$ states were examined at the Hartree–Fock level, and the geometries reported are for the lower-energy state. The CCl_3O radical[30,31] is a particularly interesting case in that neither the default CNDO nor Hückel initial guess orbitals have the symmetry of the lower-energy state, and even given starting orbitals of the correct ($^2A'$) symmetry, the DIIS convergence acceleration procedure[32] converges on an excited $^2A'$ state. Special care was required to obtain the ground state of this species. C_s symmetry was also assumed for the symmetrically substituted alcohols (CH_3OH, CF_3OH, and CCl_3OH), while no symmetry was assumed *a priori* for the other alcohols. In the latter cases both possible hydroxyl conformations were examined, and again the geometries and energies reported in Table 2 are for the lower-energy structures. As part of this investigation, the energies of the substituted methyl radicals CF_xH_{3-x} and CCl_xH_{3-x} were also required. The calculated structures and energetics of these molecules are comparable to those reported previously.[33-35]

The raw energy results for the methyl radicals, methoxy radicals, and methanols are collected in Table 3. Single-point energies were evaluated for the lowest-energy structures at the second-order Møller–Plesset (MP2) level[36] with the 6-31G(d,p) basis, keeping the core orbitals frozen. The Hartree–Fock geometries and vibrational frequencies were used to calculate zero-point vibrational energies and internal energy corrections and these are also listed in Table 3. Vibrational frequencies are in general uniformly overestimated at this level of theory;[37] to compensate for this systematic error, the frequencies were scaled by 0.9 before being used in the zero-point energy calculations. Internal translational, rotational, and vibrational energy corrections to 298.15 K were calculated using standard statistical mechanical formulas.[38,39]

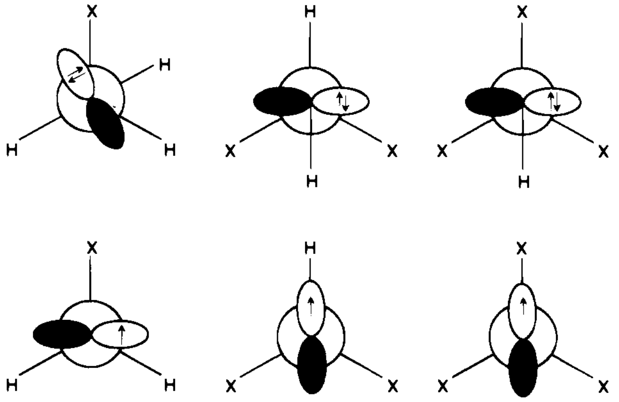

Figure 1. Newman projections along the C–O axis of $CX_xH_{3-x}OH$ (top) and $CX_xH_{3-x}O$ radical (bottom), X = F or Cl.

Results

Table 1 contains the results of geometry optimizations for the seven substituted methanols considered here. The top of Figure 1 contains Newman projections of these molecules along the C–O axis to highlight the O–H rotational orientation in each case. The lowest-energy conformation is the same for the fluorinated and chlorinated methanols with the same degree of substitution. The di- and trisubstituted methanols adopt a C_s conformation, while the monosubstituted species choose an asymmetric conformer. The energy difference between the two possible conformations of the mono- and disubstituted methanols was calculated at the RHF/6-31G(d,p) level. For CFH_2OH and CF_2HOH the energy difference between the conformers is 4.8 and 3.0 kcal mol^{-1}, respectively, while for $CClH_2OH$ and CCl_2HOH the energy difference is 4.6 and 3.3 kcal mol^{-1}. For comparison, 1,2-difluoroethane prefers a gauche over an anti conformation by 0.6 kcal mol^{-1},[40] and the barrier to rotation in

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Table 4. MP2/6-31G(d,p) Reaction and Bond Enthalpies and Estimated Heats of Formation[a]

	CH_3OH[b]	CFH_2OH	CF_2HOH	CF_3OH	$CClH_2OH$	CCl_2HOH	CCl_3OH
$\Delta_3H°_{298}$		0.9	10.8	13.7	1.9	7.3	7.2
$\Delta_4H°_{298}$		12.8	22.5	25.5	4.7	6.5	3.5
$\Delta_5H°_{298}$		11.9	11.7	11.8	2.8	−0.8	−3.6
$DH°_{298}$(RO−H)	104.4	105.3	115.3	118.2	106.3	111.7	111.6
$DH°_{298}$(R−OH)	92.5	105.4	115.2	118.3	97.3	99.2	96.4
$DH°_{298}$(R−O)	90.2	102.1	101.9	102.0	93.0	89.4	86.6
$DH°_{298}$(R−H)[b]	104.9	100.1	103.3	107.1	100.8	98.4	93.8
$\Delta_fH°_{298}$(ROH)		−103.6	−163.0	−220.7	−58.8	−66.3	−70.0
$\Delta_fH°_{298}$(RO)		−50.3	−99.7	−154.5	−4.4	−6.6	−10.4

[a] All energies in kcal mol^{-1}. [b] Experimental values from ref 42.

CH_3OH is about 1.1 kcal mol^{-1}.[41] The conformational preferences in the substituted methanols are large.

Table 2 contains the results of geometry optimizations for the seven corresponding methoxy radicals. The bottom of Figure 1 contains Newman projections along the C−O axis of these species to illustrate the orientation of the unpaired electron on the oxygen atom. All of the methoxy radicals of necessity possess C_s symmetry, but the ground state terms are not all the same. The ground and first excited states arise from the two possible distributions of three electrons in the two Oπ orbitals (oxygen p orbitals perpendicular to the C−O axis). Comparison of the methanols and methoxy radicals reveals that the ground state of the radical has a singly occupied orbital in approximately the same orientation with respect to the C−O axis as the corresponding methanol has the hydroxyl hydrogen. Thus, CF_3O has a $^2A'$ ground state, while CFH_2O has a $^2A''$ ground state. Again the chlorinated species mirror the fluorinated ones. The vertical separation between the ground and first excited states of the methoxy radicals was calculated at the UHF/6-31G(d,p) level. Across the series CFH_2O, CF_2HO, CF_3O the calculated term splitting decreases from 12.8 to 6.4 to 1.9 kcal mol^{-1}. In the analogous chlorine-substituted series, the splitting decreases from 7.8 to 5.2 to 3.4 kcal mol^{-1}. For comparison, the calculated term splitting in CH_3O is only 1.8 kcal mol^{-1}. Thus, as with the hydroxyl conformational energies, the largest term splitting is obtained in the singly substituted species, with the energy separation decreasing with increasing halogenation.

Table 3 contains the energetic results for the substituted methanols and methoxy radicals considered here. Included are the scaled zero-point and thermal contributions to the energies. The O−H bond strengths can be evaluated by considering the following isodesmic reaction:

$$CH_3O + CX_xH_{3-x}OH \rightarrow CH_3OH + CX_xH_{3-x}O \qquad (4)$$

Combining the calculated enthalpy of reaction 4 ($\Delta_4H°_{298}$) with the experimental CH_3O−H bond energy (104.4 kcal mol^{-1})[17] yields an estimate of the $CX_xH_{3-x}O$−H bond energies. The results, based on the MP2/6-31G(d,p) calculations, are collected in Table 4. As a partial validation of the computational approach, the calculations were also carried out at the MP4/6-31G(d,p) level for the CFH_2OH and CF_3OH reactions. The energetic results are essentially identical (within ±0.3 kcal mol^{-1}) to the lower-level calculations reported here. From Table 4 it is evident that halogen substitution invariably increases the O−H bond energy. The increase is not uniform, however. Addition of one fluorine or chlorine strengthens the O−H bond by only a small amount (1−2 kcal mol^{-1}), but multiple substitutions have a synergistic effect, leading to much greater bond energy increases. In the fluorine series, addition of a second fluorine increases the O−H bond strength by 10 kcal mol^{-1} and a third fluorine by an additional 3 kcal mol^{-1}. In the chlorine series, the second chlorine increases the O−H bond strength by 5 kcal mol^{-1}, but the third has essentially no effect. The non-uniform increase in bond energies suggests that the underlying source is not a simple inductive effect. We will attempt to demonstrate in the Discussion section of this work that the bond strengthening arises from the difference in effectiveness of negative hyperconjugation in stabilizing a substituted methanol and methoxy radical and that this difference is accentuated as the number of substituents is increased. As previously noted, the bond energy increase is particularly great in CF_3OH, which based on these calculations has an O−H bond energy 13.7 kcal mol^{-1} greater than that in CH_3OH. This prediction compares very satisfactorily with the earlier predicted difference of 15 kcal mol^{-1}, providing further validation of the current work.[19]

The C−O bond energies in $CX_xH_{3-x}OH$ and $CX_xH_{3-x}O$ radicals have also been examined. The CX_xH_{3-x}−OH bond energy can be obtained by considering the following isodesmic reaction:

$$CH_3 + CX_xH_{3-x}OH \rightarrow CH_3OH + CX_xH_{3-x} \qquad (5)$$

The enthalpy of reaction 5 is the difference in C−O bond energies between CH_3OH and $CX_xH_{3-x}OH$. Combining $\Delta_5H°_{298}$ with the experimental CH_3−OH bond energy (92.47 kcal mol^{-1} from the heats of formation of CH_3OH, CH_3, and OH)[42] yields an estimate of $DH°_{298}$(CX_xH_{3-x}−OH). Similarly, the C−O bond energy in the $CX_xH_{3-x}O$ radical can be derived by considering the reaction:

$$CH_3 + CX_xH_{3-x}O \rightarrow CH_3O + CX_xH_{3-x} \qquad (6)$$

which is obtained by subtracting reaction 4 from reaction 5. An estimate of $DH°_{298}$(CX_xH_{3-x}−O) can be obtained by combining $\Delta_6H°_{298}$ with the experimental CH_3−O bond energy (90.24 kcal mol^{-1} from the heats of formation of CH_3O, CH_3, and O)[42] or simply by subtracting $\Delta_4H°_{298}$ from $\Delta_5H°_{298}$. The enthalpies of reactions 5 and 6, and the calculated bond energies, are collected in Table 4. As a point of comparison, the experimentally derived CX_xH_{3-x}−H bond energies are also included in Table 4. Again as a partial validation of the computational approach, the calculations were also carried out at the MP4/6-31G(d,p) level for the CFH_2OH and CF_3OH reactions. The MP4 results are in very satisfactory agreement (±0.4 kcal mol^{-1}) with the lower-level calculations. Further, the results for the CF_3−O and CF_3−OH bond energies agree

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(41) Streitweiser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*, 2nd ed.; MacMillan: New York, 1981.

(42) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F., Jr.; Kerr, J. A.; Troe, J. *J. Phys. Chem. Ref. Data* **1992**, *21*, 1125−1568, Appendix 1.

Table 5. Mulliken Atomic Charges and Overlap Populations

	C	O	H	C−O	O−H
CH_3O	−0.040	−0.339		0.192	
CH_3OH	−0.013	−0.634	0.335	0.218	0.317
CFH_2O	0.441	−0.313		0.231	
CFH_2OH	0.473	−0.617	0.347	0.260	0.314
CF_2HO	0.887	−0.305		0.233	
CF_2HOH	0.891	−0.606	0.358	0.292	0.305
CF_3O	1.313	−0.316		0.290	
CF_3OH	1.296	−0.613	0.371	0.353	0.311
$CClH_2O$	−0.008	−0.274		0.179	
$CClH_2OH$	0.031	−0.584	0.355	0.213	0.319
CCl_2HO	−0.009	−0.235		0.145	
CCl_2HOH	0.033	−0.547	0.370	0.194	0.320
CCl_3O	−0.025	−0.208		0.097	
CCl_3OH	0.004	−0.517	0.379	0.142	0.315

reasonably well (to within 3 kcal mol^{-1}) with the previous computational results.[19]

As for the O−H bond energies, fluorine substitution results in a marked increase in the C−O bond energies. The effect is particularly pronounced for the methanols. For instance, the calculations predict the CF_3−OH bond to be a remarkable 26 kcal mol^{-1} stronger than that in CH_3OH. This difference is comparable in magnitude with the 22 kcal mol^{-1} difference in C−F bond energies between CH_3F and CF_4.[43] As with the O−H bond energies, the C−O bond energy increase is not linear in the number of attached fluorines. In fact, for the $CF_xH_{3-x}OH$ series the C−O and O−H bond energies not only follow a similar trend but are nearly equal. As a direct consequence, the CF_xH_{3-x}−O bond energies are nearly constant: $DH°_{298}(CF_xH_{3-x}{-}O)$ is uniformly 12 kcal mol^{-1} greater than $DH°_{298}(CH_3{-}O)$. That the O−H and C−O bond energies vary in such similar fashions in the substituted methanols is strongly suggestive of a single underlying mechanism accounting for both trends.

Chlorine substitution does not have as straightforward an effect on the C−O bond energies. Chlorination does increase $DH°_{298}(CCl_xH_{3-x}{-}OH)$, but the increase is not as great as in the fluorine case, and it is maximized in the disubstituted, rather than the trisubstituted, methanol. According to the calculations, CCl_3OH has the weakest C−O bond of all the halogenated methanols. Similarly, chlorination also increases the C−O bond energy in $CClH_2O$ relative to CH_3O, but further chlorination results in an apparent decrease in C−O bond strength. Chlorine is both larger and less electronegative than fluorine; the electronic effects observed with fluorine are attenuated in the chlorinated molecules and are convoluted with steric effects. However, the C−O bond energy trends in the chlorinated methoxy radicals and methanols cancel in such a way as to generate O−H bond energy trends very similar to those in the fluorinated compounds.

The heats of formation of the halogenated methanols and methoxy radicals can be estimated by combining the enthalpies of reactions 4 and 5 with the experimental heats of formation of the halogenated methyl radicals along with those of CH_3, CH_3O, and CH_3OH.[42] The results are collected in Table 4. The errors inherent in the present computational approach, combined with the uncertainties in the experimental heats of formation, make these calculated heats of formation reliable to no better than ±5 kcal mol^{-1}. Despite this large uncertainty, the heats of formation should be helpful in evaluating the potential reactions of the halogenated methanols and methoxy radicals.

Table 5 contains Mulliken population[44] information based on the HF/6-31G(d,p) wavefunctions. Included are the carbon, oxygen, and hydroxyl hydrogen atomic charges as well as the C−O and O−H overlap populations. As expected, for the methanols the carbon charges tend to increase and the oxygen charges tend to decrease with increasing halogenation. Also, congruent with the bond energy and bond length trends, the C−O overlap populations increase with increasing degree of fluorination. In contrast, the C−O overlap populations decrease with increasing chlorination for both the methoxy radicals and methanols. While the C−O overlap populations and C and O atomic charges show marked variation with the degree of halogenation, the hydroxyl hydrogen charges, and in particular the O−H overlap populations, are essentially invariant to the degree of halogenation of the alcohols. These population analysis results suggest that the "intrinsic" interaction between O and H is little perturbed by halogenation. Further study of these electron distributions using more sophisticated analysis tools is warranted.

Discussion

The results presented above illustrate the marked energetic, structural, and electronic influence that halogen substitution can have on methanols and related species. In this work our primary goal is to understand the enhanced hydroxyl bond strength in the halogenated methanols, particularly CF_3OH. As we have seen, the O−H bond energy is increased in all of the halogenated methanols relative to that in CH_3OH. The C−O bond energy is also increased in both the fluorinated methanols and methoxy radicals relative to the unsubstituted species. Our thesis is that this strengthening can be understood in terms of negative hyperconjugation effects, and the results above support this view, as we will attempt to demonstrate. In the following, we give a brief review of the negative hyperconjugation effect, and then investigate how this model can be used to understand the geometric and energetic results that have been obtained for the halogenated methanols.

Negative Hyperconjugation.[22,23] As mentioned in the introduction, the CF_3 group is known to have a strong perturbing influence on bonds β to itself. The interaction between the CF_3 group and α-bound substituents has also been extensively studied,[33,43,45−49] in particular for CF_3O radical[50] and CF_3O^-.[51,52] Because of the great electron-withdrawing ability of fluorine, the CF_3 group is generally regarded as a strong π acceptor, bonding strongly to π-donating substituents and stabilizing adjacent anionic centers. This stabilizing interaction was originally discussed in terms of double bond−no bond resonance

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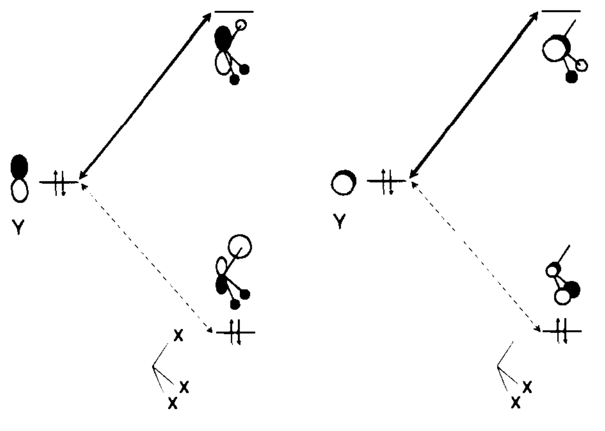
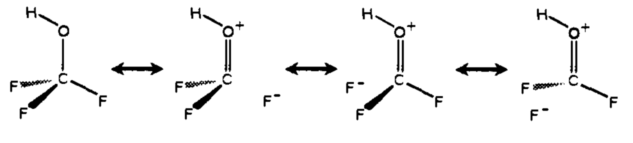


a. Symmetric interaction b. Antisymmetric interaction

Figure 2. Symmetric and antisymmetric (with respect to a vertical mirror plane) orbital interactions between a π-donor group Y and a substituted methyl group.

structures such as depicted below for CF_3OH:[53-55]



These no bond resonance structures were originally used to explain the unusual stability of CF_4. In CF_3OH their contributions are manifested in a shortened and strengthened C—O bond. As one might expect, this resonance stabilization is even more pronounced in the CF_3O^- anion, as evidenced by a very short C—O bond.[52]

The same interactions can be described in molecular orbital terms as illustrated in Figure 2 (cf. ref 22), which illustrates the interactions between a pyramidal CX_3 group and a π-donating substituent. In this description, the CX_3 group has two filled bonding and two vacant antibonding orbitals of local π symmetry arising from the individual C—X σ interactions. One pair of orbitals is symmetric and the other antisymmetric with respect to a C_s plane. A π-donating substituent CX_3—Y will have a destabilizing, 2 orbital/4 electron interaction (dotted lines) with the C—X bonding orbitals and a stabilizing, 2 orbital/2 electron interaction (solid lines) with the C—X antibonding orbitals. When X is electropositive (e.g. H), the CX_3 orbitals will be relatively high in energy and the destabilizing interactions will dominate over the stabilizing ones, weakening the bond to the substituent. When X is electronegative (e.g. F), the CX_3 orbitals will be lower in energy and the stabilizing interactions will dominate over the destabilizing ones, strengthening the bond to the substituent. The hydroxyl group has two inequivalent sets of lone pairs centered on oxygen: one of the lone pairs ($O\pi_1$, normal to the COH plane) is essentially pure p in character and can interact strongly with the CX_3 group; the other lone pair ($O\pi_2$) is in the COH plane, hybridized away from the carbon and hydrogen, and can only interact with the methyl group through its small inner lobe. Both lone pairs can interact with the CX_3 group, but to differing extents.

The double bond—no bond resonance structures introduced above correspond to a molecular orbital description with complete donation from the substituent into the C—F antibonding orbitals. These are complementary descriptions of the negative hyperconjugation effect. It is a widely, but not universally,[43] accepted model for bonding about a center with multiple electronegative substituents. The molecular orbital picture provides a more satisfactory description here, however, because the sensitivity of the effect to the orientation of the constituent species is more evident. Thus, it is clear from Figure 2 that for CFH_2 or $CClH_2$, only the symmetric interaction is possible with a π-donor substituent, and similarly for CF_2H or CCl_2H the antisymmetric interaction dominates negative hyperconjugation, although a weaker symmetric interaction is also possible. These orientational dependencies can be used to understand the energetic and geometric energetic trends found in the halogenated methanols, which we now discuss.

Molecular Geometries. Across the series CH_3OH, CFH_2OH, CF_2HOH, CF_3OH the C—O bond length decreases markedly (0.069 Å from CH_3OH to CF_3OH, see Table 1). In the same series, the O—H and C—H bond distances are essentially invariant, but the C—F bond distances also decrease significantly (0.057 Å). Analogous trends are present in the chloride series, although the magnitude of variation is not as great. These trends are similar to those well-known in the CF_xH_{4-x} series, first noted by Brockway.[53] They have been taken as evidence for negative hyperconjugation in CF_xH_{4-x},[45] although Wiberg and co-workers have contended that it is primarily a Coulombic effect.[43] In either case, based on bond length trends alone, the interaction between the hydroxyl and methyl groups appears to increase with increasing halogen substitution, consistent with the bond energy trends and with the expected influence of negative hyperconjugation. If hyperconjugation between the methyl and hydroxyl groups is important, one might also anticipate the C—O—H angle to open up across the series of increasing halogenation. Such a trend is in fact observed, but the angle variations are fairly small (<1° change from CH_3OH to CF_3OH).

Further evidence for the importance of negative hyperconjugation in the substituted methanols is provided by the calculated relative conformational energies. These energies vary in a manner consistent with that noted in other systems in which negative hyperconjugation is important.[23] As illustrated in Figure 1, for both the fluorinated and chlorinated methanols, the lowest energy conformation is consistently the one with the hydroxyl hydrogen gauche to the maximum number of halogens, despite the obvious steric penalty incurred for adopting such a position. This preference is so great in CFH_2OH that the trans conformer is actually a saddle point for rotation about the C—O bond rather than a minimum.[56] In all cases, the gauche orientation of the hydroxyl group is consistent with a tendency to maximize the interaction between $O\pi_1$ (the essentially unhybridized $O\pi$ orbital) and the halogens: in the singly substituted methanols, it is a symmetric interaction as illustrated in Figure 2a; in the doubly substituted methanols, it is primarily an antisymmetric interaction, as illustrated in Figure 2b. As noted above, the energetic preference is slightly greater in CFH_2OH than in CF_2HOH, and similarly greater in $CClH_2OH$ than in CCl_2HOH. Rotation away from the optimal conformation not only diminishes the stabilizing interaction between $O\pi_1$ and the halogens but also increases the destabilizing interaction between $O\pi_1$ and the high-energy C—H orbitals. This destabilizing influence is more important in the singly substituted species because of the greater number of C—H bonds.

The geometric trends for the methoxy radicals are substantially different than those noted in the methanol molecules above. Excepting the CH_3O radical, as the degree of substitution

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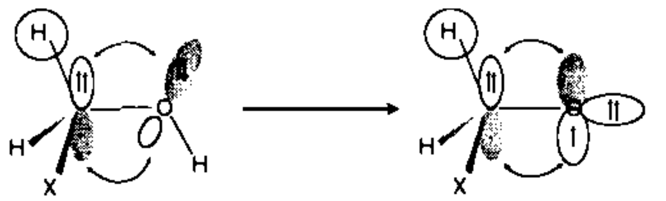
at the methyl group increases, the C−O bond length also increases. In contrast, the C−X bond distances decrease with the degree of substitution, just as noted for the methanols. The change in bond distances is not nearly as great in the methoxy radicals as it is in the methanols (<0.01 Å, from CFH_2O to CF_3O) but the trend is evident. It suggests that the interaction between the methyl group and the attached oxygen diminishes slightly with increasing substitution. It is suggestive of a decrease in hyperconjugative stabilization in the methoxy radicals.

More revealing is the comparison between the C−O bond lengths in the methanols and corresponding methoxy radicals. For CH_3OH, CFH_2OH, and $CClH_2OH$, removal of the hydroxyl hydrogen results in a marked *decrease* in the C−O bond length. In these three species, substantial destabilizing interactions of the type illustrated in Figure 2 exist between one or both of the hydroxyl lone pairs and the relatively high energy C−H bonding orbitals. This destabilizing interaction is relaxed in the radical, as one of the lone pairs rotates away from the methyl group and is replaced (essentially) by an unpaired electron:



The decrease in the destabilizing interaction allows the C−O bond to contract. In contrast, for CF_3OH and CCl_3OH, and to a lesser extent CF_2HOH and CCl_2HOH, removal of the hydroxyl hydrogen results in an *increase* (or at least no change for CCl_2HOH) in the C−O bond length. In these molecules, both $O\pi_1$ and $O\pi_2$ can interact with the methyl group in a stabilizing fashion, $O\pi_1$ strongly through an antisymmetric interaction, and $O\pi_2$ more weakly through a symmetric interaction. In the corresponding radicals, the symmetric interaction is diminished as an unpaired electron replaces the $O\pi_2$ lone pair of electrons. Unlike the case above, however, this loss results in a net destabilization of the C−O bond and a corresponding increase in the C−O bond length. This bond length increase is particularly pronounced in moving from CF_3OH to CF_3O radical, for which changes in negative hyperconjugation are expected to be most significant.

All of the calculated geometric trends in the halogenated methanols and methoxy radicals are thus consistent with the predicted consequences of the negative hyperconjugation model.

Radical State Separations. The importance of negative hyperconjugation in the methoxy radicals is further reinforced by considering the energetic separation between their ground and first excited states. This splitting decreases precipitously across the series CXH_2O, CX_2HO, CX_3O and can be readily understood in terms of the interactions of the singly and doubly occupied $O\pi$ orbitals with the substituted methyl group. In the ground state of the CXH_2O radical (Figure 1), the doubly occupied $O\pi$ orbital is oriented to interact in a stabilizing, symmetric fashion with the CXH_2 group, while the singly occupied $O\pi$ orbital interacts in a weakly destabilizing, antisymmetric fashion with the C−H bonds of CXH_2. In the first excited state, which corresponds to an interchange of the singly and doubly occupied $O\pi$ orbitals, the situation is exactly reversed. The doubly occupied $O\pi$ orbital interacts strongly in a destabilizing fashion with the C−H bonds, and only a single electron is able to participate in the stabilizing symmetric interaction. This asymmetry in the orbital interactions leads to the large energetic separtion in the ground and first excited states. A similar situation holds in CX_2HO, but because some of the stabilizing hyperconjugation is retained in the excited state and because the destabilizing interaction is with only one C−H bond, the state splitting is not as great. In CX_3O (X = F, Cl, *or* H), the hyperconjugative interactions (or absence thereof) are essentially the same in the ground and excited states, and the energetic separation between the two is small.

Again, the negative hyperconjugation effect provides a ready explanation for the state orderings in the methoxy radicals. It is difficult to imagine a similar explanation for these energy separations based upon simple Coulombic or inductive effects.

Hydroxyl Bond Energies. Based on the structural and energetic information discussed above, the methanol/methoxy radical pairs can be segregated into two distinct groups. The first group includes CH_3OH, CFH_2OH, and $CClH_2OH$. The O−H bond strengths are roughly the same in this group. They all have relatively long C−O bonds, and as permitted by symmetry they show a marked energetic preference for one hydroxyl conformation. Abstraction of the hydroxyl hydrogen results in a decrease in the C−O bond length, and the splitting between the ground and first excited states of the corresponding methoxy radicals is large. The second group includes all the di- and trihalogenated methanols CX_2HOH and CX_3OH, which exhibit opposite characteristics. These species are all predicted to have O−H bond strengths significantly greater than the members of the first group. They have relatively short C−O bonds, and the energetic preference for a particular hydroxyl group orientation is smaller than in the first group. Their C−O bond lengths increase upon removal of the hydroxyl hydrogen, and the splitting between the ground and first excited states of the resultant methoxy radicals is relatively small.

As we have seen, the geometric trends are readily understood in terms of the negative hyperconjugation model. The same is true of the hydroxyl bond energies. Individual bond energies in any molecule are determined by the difference in stability of the parent molecule and the daughter radical species. In the halogenated methanols, it is the difference in stability of the methanol and methoxy radical that determines the O−H bond energy. One convenient way to measure the relative stability of these two is in terms of differences in their C−O bond energies. From eq 3 this difference is directly related to the O−H bond energy. In the molecules studied here, the C−O and O−H bond energies generally increase with the degree of halogenation. However, the patterns are consistent with the role of negative hyperconjugation originally postulated for CF_3OH.[19]

In the first group of compounds discussed above, including CH_3OH, CFH_2OH, and $CClH_2OH$, negative hyperconjugation between the hydroxyl and methyl groups is either limited to one molecular plane or absent altogether, and removal of the hydroxyl hydrogen results in little change in this interaction. The difference in stability of the methanol and methoxy radical, as measured by the C−O bond energy difference $DH^\circ(R{-}OH) - DH^\circ(R{-}O)$, is expected to be roughly constant for these three compounds. As a consequence the O−H bond energies will also be nearly constant (see eq 3), as confirmed by the calculations. Qualitatively, a single halogen substituent can stabilize only one $O\pi$ electron pair. Both the methanol and methoxy radical have an oxygen lone pair available to interact with this halogen. Both species are stabilized a similar amount by negative hyperconjugation, and as a result the stabilization has no net effect on the energy of the methanol O−H bond.

In contrast, in the second group of compounds, including CF_2HOH, CF_3OH, CCl_2HOH, and CCl_3OH, negative hyperconjugation has a large stabilizing influence on the parent methanols, and removal of the hydroxyl hydrogens results in an electronic reorganization that significantly diminishes the hyperconjugative interaction. The C−O bond energy difference DH°(R−OH) − DH°(R−O) is thus expected to be much larger in this group, and consequently the hydroxyl bond energies will also be larger. Qualitatively, multiple halogen substituents can interact with and stabilize two Oπ 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. The resulting difference in stabilization is manifested in an apparently enhanced O−H bond strength, even though the O−H bond is not directly perturbed by the halogens. Again this expectation is confirmed by the calculations. Based on this explanation, if the O−H bond is cleaved heterolytically rather than homolytically, so that the oxygen maintains a full complement of lone pairs, the resulting anion will be slightly more stabilized by negative hyperconjugation than the parent molecule, and gas-phase acidity will be enhanced. This same result is expected independent of the number of halogen substituents, so a non-uniform increase in acidity with the number of substituents is not expected. Inductive effects will dominate the acidity of substituted methanols, and as a result the acidity is expected to increase roughly linearly with the number of substituents.

A further test of this theory is possible using the computed results. Negative hyperconjugation in CXH_2O, and to a lesser extent CX_2HO and CX_3O, radicals is partially blocked in the first excited states of these species. The loss of negative hyperconjugation implicated in enhancing the CX_3O−H bond strengths can be induced in the partially substituted methanols by referencing the bond energies to the methoxy radical excited states rather than ground states. Using the calculated vertical Hartree−Fock excitation energies, the "adjusted" O−H bond energies for CFH_2OH, CF_2HOH, and CF_3OH are 118.1, 121.7, and 120.1 kcal mol^{-1}, respectively. Using this artificial reference state, then, the O−H bond energies are found to be nearly constant. Similar results are obtained for the chlorinated species: 114.1, 116.9, and 115.0 kcal mol^{-1} for the O−H bond energies in $CClH_2OH$, CCl_2HOH, and CCl_3OH, respectively. Thus, referenced to a state in which negative hyperconjugation is restricted, halogenation has a constant stabilizing effect on the O−H bond energies. While not proof, this observation provides further evidence of the role of negative hyperconjugation in strengthening the O−H bonds.

In summary, then, the increase in hydroxyl bond strength with increasing halogenation can be traced to differences in the stability of the parent methanol and methoxy radical that are attributable to differences in the effectiveness of negative hyperconjugation in the two. The magnitude of this effect is dramatic; it leads to the greatly enhanced O−H bond strength previously noted in CF_3OH.[15] These results confirm our earlier hypothesis that variations in negative hyperconjugation can be used to explain the β bond energy variations in halogenated methanols.

Conclusions

We have examined the C−O and O−H bond energy trends in the series of fluorinated and chlorinated methanols. According to the calculations, halogenation is invariably found to strengthen these bonds, often to a surprisingly large extent. As previously discussed, the O−H and C−O bonds in CF_3OH are particularly robust compared to those in CH_3OH.

We have attempted to demonstrate that the calculated changes in molecular structure and bond energies with degree of halogenation can be understood in terms of the negative hyperconjugation effect and its dependence on molecular and electronic structure. One of the most interesting aspects of these results is that negative hyperconjugation in $CX_xH_{3-x}OH$, which is in principle an effect localized in the C−O and C−X bonds sharing a common center, can be manifested so dramatically in O−H bonds β to the carbon center. The unusual stability of the CF_3O−OCF_3 and CF_3O−OH bonds can undoubtedly be traced to the same effects, and we expect that there are many other examples. While other interpretations of these results may be possible, the negative hyperconjugation model, which previously has been applied to conformational and α bond energy effects, can be used quite successfully to explain the dramatic variation in β bond energies in the halogenated methanols. The bond energy trends noted here provide another means to investigate the role of negative hyperconjugation in other systems.

It is appropriate to consider the practical implications of these results. With the exception of CF_3OH, none of the halogenated methanols considered here are anticipated to play a significant role in the atmospheric chemistry that originally motivated this work. As already described, CF_3OH is formed in the atmosphere primarily by reaction of the CF_3O radical with methane (reaction 1) or water (reaction 2). On the basis of the calculated O−H bond energies, similar reactivity might be anticipated for CF_2HO, CCl_2HO, or CCl_3O. However, di- and trichlorinated alkoxy radicals are known to rapidly eliminate chlorine atoms to generate carbonyl compounds.[57] Similarly, alkoxy radicals with α hydrogens react readily with molecular oxygen, also to produce carbonyl products, for example:[58]

$$CF_2HO + O_2 \rightarrow COF_2 + HO_2 \qquad (7)$$

Thus, only for the CF_3O radical, for which these alternate modes of decomposition are unavailable, is reaction with hydrogen donors in the atmosphere likely, and is CF_3OH chemistry important. As we have shown here, however, the chemistry of the other substituted methanols can shed valuable light on the behavior of the CF_3O/CF_3OH system. All of the substituted methanols reported here can be prepared in the gas phase in the laboratory, and although the chlorinated methanols,[24] as well as CF_3OH,[59] are known to decompose with loss of HX

$$CX_xH_{3-x}OH \rightarrow COX_{x-1}H_{3-x} + HX \qquad (8)$$

it may be possible to examine the structures and O−H bond strengths in some of these compounds experimentally, as well as to examine the excitation energies of the methoxy radicals spectroscopically. Further experiments are underway in our laboratory.

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