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Weak Acidity of Vinyl CH Bonds Enhanced by Halogen Substitution

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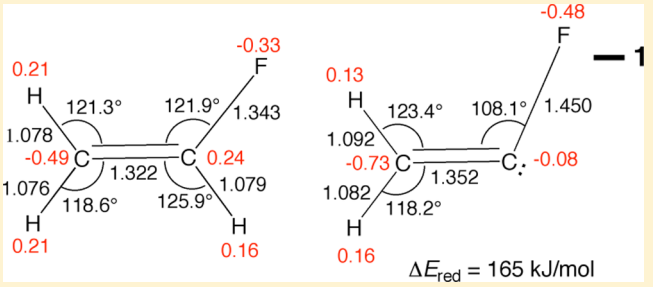
Supporting Information

ABSTRACT: As shown by the rates of proton−deuteron exchange in ethylenes with halogen substituents, the weak acidity of vinyl CH bonds is enhanced by halogen substitution. Relative rates of exchange in basic deuterium oxide reflect the relative acidities. Substitution in the α position has the strongest effect. Less electronegative halogens such as bromine increase the acidity more than does fluorine. The vinyl CH acid strengths correlate closely with the energies of deprotonation of isolated molecules into isolated anions, as computed with the MP2/cc-pVQZ model. The smaller deprotonation energies are associated with the stronger acids. Atomic charges from a natural bond order analysis done with the MP2/aug-cc-pVQZ model show that the negative charge becomes more dispersed in the anions of the stronger acids. Results are given for 13 haloethylenes and for 6 halogen-substituted butadienes, cyclopropenes, and a cyclobutene.



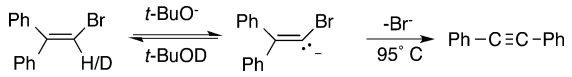
INTRODUCTION

Missing from compilations of acid strengths are substances having vinyl CH bonds made weakly acidic by halogen substituents.[1−3] Previously, studies of relative rates of proton−deuteron exchange chemistry, the method of *kinetic acidity*,[2] have been used to determine pK_a's of weakly acidic CH bonds in nonaqueous solutions. In this paper, we report a qualitative ranking of acid strengths of vinyl CH bonds enhanced by halogen substitution as determined from proton−deuteron exchange chemistry in aqueous solutions. This chemistry was inspired by the early work of Francis and Leitch on the exchange of trichloroethylene with basic deuterium oxide[4] and the work of Miller and Lee on the exchange of 1,2-dibromoethylene-d_2 in sodium methoxide−methanol.[5] The latter workers also exchanged *cis*- and *trans*-1,2-dibromoethylene, *cis*- and *trans*-1,2-dichloroethylene, *trans*-1,2-diiodoethylene, and tribromoethylene in basic deuterium oxide at various temperatures.[5] Miller and Lee found a pK_a of 34 for dibromoethylene in methanol.[5] Since then, we have used many exchange reactions in basic deuterium oxide to make substances with specific deuterium substitution. This synthetic chemistry is scattered in the spectroscopic literature (see Table 1 below). In this paper, we assemble these data, identify noteworthy patterns of acidity, and use quantum chemical (QC) calculations to investigate reasons for these often surprising findings. The substances are mostly haloethylenes supplemented with some halogen-substituted butadienes, cyclopropenes, and a cyclobutene.

Richard and co-workers reported quantitative studies of acidities of weak CH acids in water studied by the kinetic method. Most had sp^3 CH bonds activated by neighboring CO and CN bonds.[6] They found pK_a's for these species. None of the examples involved halogen substitution.

α-Halovinyl anions have been invoked as intermediates in the Fritsch−Buttenberg−Wiechell (FBW) rearrangement of haloethylenes to acetylenes.[7−10] The FBW rearrangement is believed to proceed by the base-induced α-elimination of HX to give a carbenoid intermediate, which rearranges to an acetylene. Pritchard and Bothner-By investigated the rearrangement of 2,2-diphenyl-1-bromoethylene to diphenylacetylene in the presence of potassium *tert*-butoxide in *tert*-butyl alcohol-*d* at 95 °C (Scheme 1).[11]

Scheme 1



They observed that the starting material underwent H−D exchange faster than formation of the acetylene. Running the reaction at 35 °C resulted in only H−D exchange and no rearrangement products. Hartlzer has also reported that halogens increase the acidity of allenes.[12] Treatment of 1-chloro-3-methyl-1,2-butadiene with *tert*-butoxide at 0 °C resulted in the α-elimination of HCl to give a carbenoid, which was trapped with olefins (Scheme 2).

Scheme 2

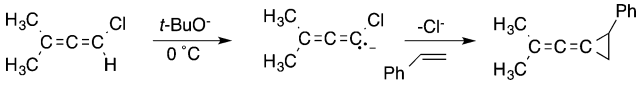


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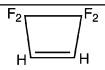
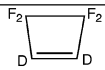
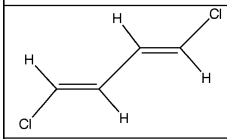
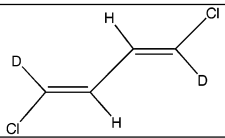
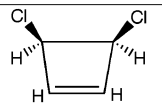
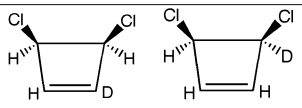
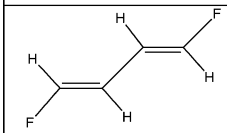
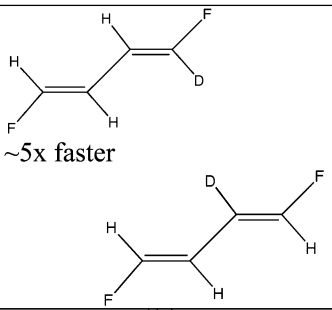
Table 1. Rate of Exchange of Deuterium for Hydrogen in Descending Order of CH Acid Strength

	Product	Conditions[a]	Reference
		2 M, RT, mins	Ref 13
		3 M, RT, mins	Ref 14
Br_2C=CBrH	Br_2C=CBrD	1-2 M, 25°C, 2 h	Ref 5
HBrC=CBrH	DBrC=CBrD[b]	1-2 M, 25°C, 55 h	Ref 5
		0.3 M, 50°C, 12 h	Ref 15
FClC=CClH	FClC=CClD	CaO, 75°C, 12h	Ref 16
Cl_2C=CClH	Cl_2C=CClD	2 M $Ca(OD)_2$, 87°C, 12 h	Ref 5 This work[c]
H_2C=CBrH	H_2C=CBrD[d]	1.5 M, 65°C, 3.5 d	Ref 17
Cl_2C=CFH	Cl_2C=CFD	CaO, 95°C, 12 h	Ref 18
HClC=CClH	DClC=CClD[e]	2 M, 80°C, 41 h	Refs 5, 19
		2 M, 91°C, 74 h	Ref 20
FClC=CFH	FClC=CFD	CaO excess, 85°C, 2.5 d, ~10 atm	Ref 21
HClC=CFH	DClC=CFD[e,g]	CaO excess, 125°C, ~10 atm, 1 d	Ref 22
F_2C=CFH	F_2C=CFD[f]	3 M, 100°C, 3 d	This work
HFC=CFH	DFC=CFD[e]	2 M, 90°C, 2 d	Ref 23
	 ~2x faster	3 M, 100°C, 24 h ~5% conversion	Ref 24
	 ~5x faster	3 M, 120°C, 10 d for 1/3 protons exchanged	Ref 25
H_2C=CFH	H_2C=CFD[d,h,i]	3 M, 120°C, 8 weeks	Ref 17

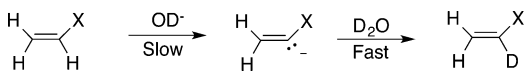
[a]NaOD/D_2O unless otherwise indicated. For the weaker acids, the time given is for an incomplete exchange. [b]Also studied in sodium methoxide/methanol. [c]The reaction in OH^-/CH_3OD was studied quantitatively by NMR for a physical chemistry experiment. [d]Acetylene is a byproduct. [e]Exchange shown to be stereospecific. [f]Judged more acidic than HFC=CFH despite the apparent exchange rate because the lower boiling point of F_2C=CFH implies smaller solubility. [g]The Cl-substituted end exchanges faster than the F-substituted end. [h]Small amount of exchange on the CH_2 end. Exchange halted at approximately 2/3 because of this additional exchange and the loss to acetylene formation. [i]Exchange of H_2C=CFH was also observed by Kurt A. Hillig II at 135 °C. He obtained a mixture of isotopic species for use in microwave spectroscopy. This observation was reported in his Ph.D. thesis at the University of Michigan in 1981.

RESULTS AND DISCUSSION

The exchange chemistry reported here is characterized by the reaction sequence in Scheme 3.

Halogen atoms may be substituted in various numbers, α or β. The rate-determining step, which is the proton removal by OD^- in an aqueous phase, reflects the acid strength of the CH bond. In a fast second step, the carbanion extracts deuterons from the abundant deuterium oxide solvent.[6] A potential competing reaction is α-elimination of a hydrogen halide to give acetylene (FBW rearrangement in Scheme 4).[10]

Scheme 3



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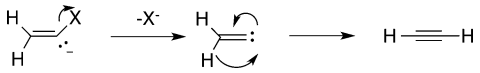
Scheme 4



However, none of this alternative chemistry occurs for most of the examples cited here despite many hours of reaction at temperatures mostly in the 100−120 °C range with OD^- concentrations of 2−3 M. All of the substances studied were quite resistant to other side reactions under the specific reaction conditions.

Table 1 gives a qualitative ranking of the relative acidities based on the rate at which the exchange reaction took place. The strongest CH acids are at the top of the table, and the weakest acids are at the bottom. In two cases where some acetylene formed by elimination, the exchanges of 1-bromoethylene and 1-fluoroethylene, the acetylene was fully deuterated early in the process, showing that the acidity of acetylene was greater than any of the species in Table 1.

Surprises are found in the relative acidities in Table 1. The α-substitution of a bromine atom in ethylene produces a faster rate of exchange than does α-substitution of a fluorine atom. The effect of chlorine substitution is intermediate. Thus, monobromoethylene is more acidic than monofluoroethylene. This pattern is directly discernible in the rate of exchange of the two ends of the 1-chloro-2-fluoroethylene molecule, where the CClH end exchanges appreciably faster than the CFH end. The corresponding comparison is not available for 1-bromo-2-fluoroethylene but can be expected to follow the pattern of the CBrH end being more acidic. More halogen substituents increase the acidity with the less electronegative halogen substituents having the greater effect. Thus, tribromoethylene is more acidic than trifluoroethylene. Substituting a chlorine atom in the β position to a CFH bond gives greater acid strength than does substituting a fluorine atom. This distinction is seen in comparing the rankings of 1,2-difluoroethylene and the CFH end of 1-chloro-2-fluoroethylene. Overall, the acid-enhancing effect of a less electronegative halogen atom is greater in both α and β substitution. The effect on CH acidity of local halogen substitution is somewhat greater in butadienes than in ethylenes. In 1,4-dichlorobutadiene exchange occurs only at C1 and C4. In comparison, 1,4-difluorobutadiene is significantly less acidic, and exchange occurs ∼5× faster at C1 and C4 than at the interior CH bonds at C2 and C3.

We have investigated these patterns of acidity with QC calculations of the energies of deprotonation of the isolated acid molecules. The moderate-level MP2/cc-pVQZ QC model was applied with the Gaussian software package.[26] Optimized energies and structures were computed for the acid species and for the corresponding anions with the acid proton at infinity. Table 2 gives the computed *reduced* energy differences (red) for proton affinities (ΔE_{red}) in kJ/mol, for which 1500 kJ/mol was subtracted to put the differences in sharper relief. In Table 2 the order of the ethylene entries is generally in the sense of decreasing proton affinity, i.e., increasing acidity. Exceptions are where different isomers are grouped together. A few of the entries in Table 1 are not in Table 2. Table S1 (Supporting Information) gives calculated energies (in hartrees/particle) of each species at the MP2/cc-pVTZ as well as at MP2/cc-pVQZ level. The less expensive MP2/cc-pVTZ calculations were done as a preliminary exploration. Concerned that diffuse functions might be needed, especially for the anion with an unshared electron pair, we did another, smaller set of expensive calculations at the MP2/aug-cc-pVQZ level for the species to be stressed in this paper. The results of these calculations are included in Table S1 (Supporting Information). As expected, bond lengths differ less than 0.01 Å, except for the CCl and CBr bonds where differences are up to 0.04 Å, between the three levels of theory. Energies are more sensitive to the basis set. The pattern of energy *differences* is similar for the three models, but the cc-pVTZ basis set gives energy differences approximately 15 kJ/mol larger than the cc-pVQZ basis set, which, in turn, gives values approximately 15 kJ/mol larger than the aug-cc-pVQZ basis set. Atomic charges were determined at the MP2/aug-cc-pVQZ level of theory with the natural bond order (NBO) package within G09.[26,27]

Table 2. Reduced Proton Affinities (ΔE_{red})[a] from the MP2/cc-pVQZ Model

species	ΔE_{red} (kJ/mol)	species	ΔE_{red} (kJ/mol)
$H_2C{=}CH{:}-$	256.8	$Cl_2C{=}CCl{:}-$	58.9
$H_2C{=}CF{:}-$	183.8	*cis*-HBrC=CBr:−	62.5
cis-HFC=CH:−	192.4	*trans*-HBrC=CBr:−	70.4
trans-HFC=CH:−	186.0	$Br_2C{=}CBr{:}-$	35.0
$H_2C{=}CCl{:}-$	141.6		
cis-HFC=CF:−	146.0	$H_2C{=}CH{-}CH{=}CH{:}-$ *Z*	215.8
trans-HFC=CF:−	146.2	$H_2C{=}CH{-}CH{=}CH{:}-$ *E*	220.6
$F_2C{=}CF{:}-$	121.6	$H_2C{=}CH{-}C{:}-{=}CH_2$	214.7
$H_2C{=}CBr{:}-$	124.6	*EE*-HFC=CH−CH=CF:−	134.6
Z-HFC=CCl:−	109.5	*EE*-HFC=CH−C:−=CFH	138.7
Z-HClC=CF:−	118.8	EE-HClC=CH−CH=CCl:−	91.8
E-HFC=CCl:−	105.4	*EE*-HClC=CH−C:−CClH	118.8
E-HClC=CF:−	129.5		
Z-HFC=CBr:−	95.3	cyclopropene:− (=C:−) CP	151.9
Z-HBrC=CF:−	105.3	cyclopropene:− (CH:−)	306.6
E-HFC=CBr:−	91.2	3,3-F_2CP:− (=C:−)	70.6
E-HBrC=CF:−	123.5	1,3,3-F_3CP:− (=C:−)	30.1
cis-HClC=CCl:−	87.6		
trans-HClC=CCl:−	91.5	HCC:−	118.5

[a]Calculated proton affinity with 1500 kJ/mol subtracted.

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The pattern of proton affinities in Table 2 with the smaller value corresponding to the stronger CH acid follows the ranking of qualitative acidities in Table 1 remarkably well.

Included in Table 2 are proton affinities for unsubstituted ethylene, butadiene, cyclopropene, and acetylene. Except for acetylene, each of these pure hydrocarbons has a much larger ΔE_{red} than its corresponding halogen-substituted species. ΔE_{red} for acetylene falls in the middle of the values for the haloethylenes, whereas acetylene is more acidic than any of the CH acids in Table 1. Calculation of ΔE_{red} for acetylene at higher levels of theory (Table S1, Supporting Information) gave similar values for ΔE_{red}. A likely explanation for the discordant value of ΔE_{red} for acetylene compared to its significant acidity is a more favorable ionization energy for the small $HCC:^-$ anion in water in comparison with other species investigated. This anion is much smaller than any of the others and thus would hydrate more strongly, thereby favoring ionization of acetylene.

Of course, several assumptions are involved in making the association of ΔE_{red} with acid strength. Energy differences are being used rather than ΔG values, which relate to equilibrium constants. Thus, entropy differences are regarded as remaining roughly the same across a range of acid molecules and basic anions that are similar in size in both reactants and products. It is also assumed that the rate of the rapid reprotonation process is nearly constant across the series.[6] Finally, the hydration energy contributions, especially to anions, are regarded as comparable, except for acetylene. The strong correlation between the relative rates of exchange and the energy differences supports interpreting the ΔE_{red} as a useful correlation with the acid strength of CH bonds in the substances under consideration.

Changes in bond lengths and NBO atomic charges give insight into the observed ranking of acidities of CH bonds. We employ this approach with caution because no rigorous way exists to obtain atomic charges from QC calculations, even though the use of the NBO atomic charges has been recommended by Wiberg and Rablen.[28] Figures 1−3 give NBO atomic charges (in red color), bond lengths, and ΔE_{red} as computed with the MP2/aug-cc-pVQZ model that includes diffuse functions in the basis set.

In Figure 1, bond parameters and NBO atomic charges are shown for 1-fluoroethylene, 1-chloroethylene, and 1-bromoethylene and their corresponding anions. The negative charge is more dispersed in amount and in space in the bromoethylene anion than in the fluoroethylene anion compared to the corresponding acids, thereby favoring the formation of the bromoethylene anion from its conjugate acid relative to the formation of the fluoroethylene anion from its conjugate acid. The fairly large charge separation in fluoroethylene has little flexibility left for further separation in the anion. In contrast, the smaller charge separation in bromoethylene can be substantially enhanced through anion formation. In addition, the CH bond in fluoroethylene has an unfavorable polarity for deprotonation compared to the CH bonds in chloroethylene and bromoethylene. CX bond lengths increase substantially in forming the anions. For example, in ionizing fluoroethylene the CF bond length increases 0.107 Å; in deprotonating bromoethylene the CBr bond length increases 0.173 Å. Overall, the bromoethylene molecule is able to increase in size more with deprotonation than the fluoroethylene molecule and therefore disperse the negative charge more effectively. The chloroethylene species is intermediate. With deprotonation the NBO atomic charges on

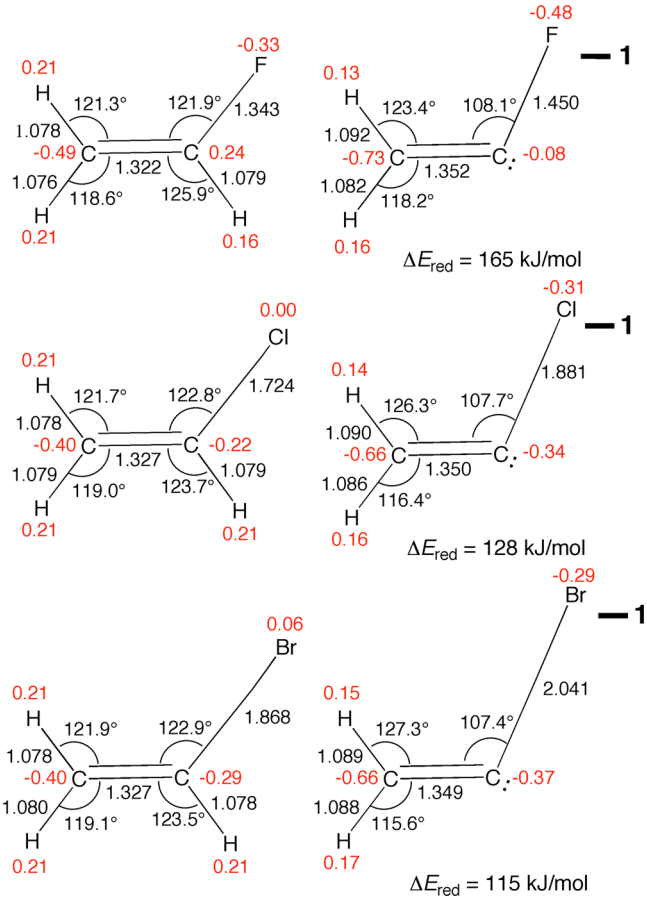

Figure 1. Structures, NBO atomic charges, and ΔE_{red} of ionization for three monohaloethylenes; MP2/aug-cc-pVQZ model.

the carbon atoms change significantly in the negative sense as they do on the halogen atoms. However, the negative charge on the deprotonated carbon atom is surprisingly small, as this charge is dispersed over the whole ion. Even the hydrogen atoms gain some in less positive atomic charges in the anions.

In each of the anions, the bond angle for the C═C−X sequence undergoes a large decrease of 10−15° when a proton is removed from this end of the molecule. This decrease in bond angle in the anions reflects a significant rehybridization of the carbon orbital for the C−X bond to have more *p* character. The trend in the *p* character from 85% to 90% to 92% for the F → Cl → Br sequence verifies this interpretation and correlates with the increase in acid strength.[30] In none of the species does the C═C bond length increase more than 0.03 Å in the deprotonation process. The *s* character in the lone pair orbital of the anion goes from 50% to 54% to 57% for the F → Cl → Br sequence,[30] an outcome that is consistent with the trend in acid strength. Changes in bonding are principally in the single σ bonds, especially those involving halogen atoms. The charge separations for the CH bonds change from 0.08 to −0.43 to −0.50 for the sequence F → Cl → Br. Thus, the CH bond becomes more polar in the acidic sense in going from fluoroethylene to bromoethylene.

As noted in the survey of the experimental results, a direct comparison of the effect of a local halogen-atom substitution is provided by 1-chloro-2-fluoroethylene. The chlorine-substituted end is more acidic than the fluorine-substituted end as reflected in the faster rate of exchange on the CClH end. Figure 2 compares the bond parameters and the NBO atomic charges

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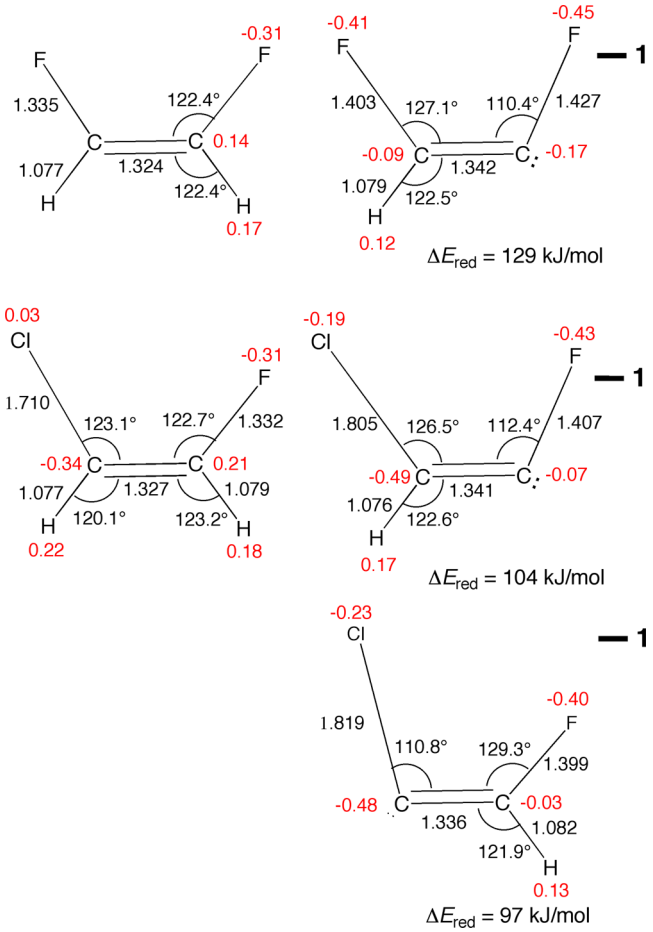

Figure 2. Structures, NBO atomic charges, and ΔE_{red} of ionization for two dihaloethylenes; MP2/aug-cc-pVQZ model.

for the acid and anion species of *cis*-1,2-difluoroethylene and of *Z*-1-chloro-2-fluoroethylene upon deprotonation of both ends. ΔE_{red} for deprotonation of the Cl end of *Z*-1-chloro-2-fluoroethylene is smaller by 7 kJ/mol than for the CF end, and ΔE_{red} for deprotonation of the F end of *Z*-1-chloro-2-fluoroethylene is smaller by 25 kJ/mol than for *cis*-1,2-difluoroethylene. Thus, local and distant Cl substitution increases the CH acidity. Local substitution has the larger effect. The energy differences are consistent with the qualitative acidity rankings in Table 1. The local effect of chlorine substitution is similar to that in chloroethylene. By comparing the changes in bond lengths and atomic charges accompanying deprotonation in Figure 2, it is apparent why adding the chlorine atom β has a greater effect than adding a fluorine atom β. A more significant change in the negative charge occurs on the β chlorine than occurs on the already electron-rich β fluorine atom.

Figure 3 shows two examples of the effect on acidity of multiple halogen atom substitution. Tribromoethylene is much more acidic than trifluoroethylene as is seen in the qualitative rankings of acidities in Table 1 and in the relative ΔE_{red} values of 105 kJ/mol for the fluorine species and 31 kJ/mol for the bromine species in Figure 3. Charge changes on the bromine atoms are larger than on the fluorine atoms, and the longer C−Br bonds disperse the negative charge more than do the shorter C−F bonds.

For several of the examples of exchange in Table 1, stereospecificity was confirmed. These examples include 1,2-

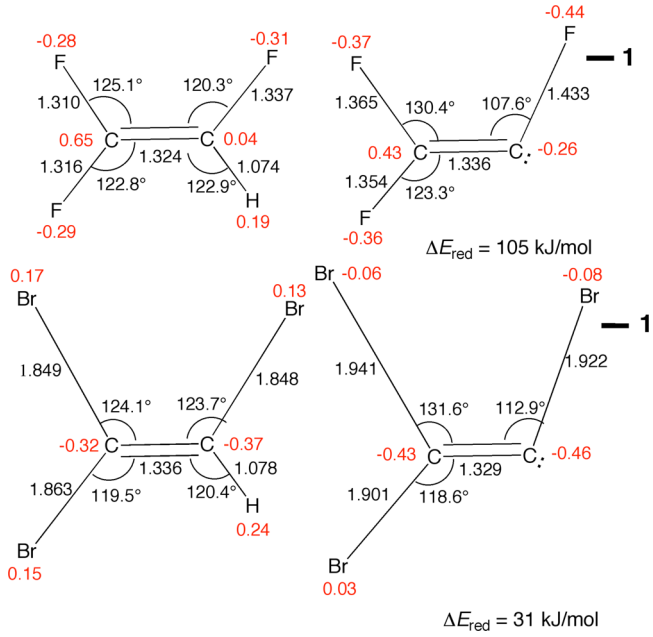

Figure 3. Structures, NBO atomic charges, and ΔE_{red} of ionization for two trihaloethylenes; MP2/aug-cc-pVQZ model.

dichloroethylene, 1,2-difluoroethylene, 1-chloro-2-fluoroethylene, 1,4-dichlorobutadiene, 1,4-difluorobutadiene, and 3,4-dichlorocyclobutene. Stereospecificity for the exchange of 1,2-dichloroethylene was also reported by Miller and Lee.[5] Thus, we presume that stereospecificity is characteristic of all the exchange reactions. Stereospecificity implies localization of the unshared electron pair left upon deprotonation, despite the small negative NBO atomic charges at this site in the anions. A computed map of electrostatic charge shows, for example, with the chloroethylene anion,[26] that the highest negative potential is where the unshared pair of electrons is located, thereby correlating with the observation of stereospecificity in the exchange reactions. This observation is a good reason for caution about the absolute atomic charges. However, *changes* in atomic charges upon deprotonation are regarded as useful for interpreting the relative acidities.

Some attempted exchanges did not succeed under the conditions reported here. Miller and Lee also reported a number of exchanges that did not occur for substituted ethylenes.[5] Cyclooctatetrene (COT), which should be comparable to ethylene in acid strength, did not exchange even though it survived for many days in contact with strong aqueous base up to 110 °C and with tetrahydrofuran added to increase solubility of COT in the water phase. The sp^3 CH bond of the HCOH group did not exchange in 1,5-hexadien-3-ol, nor did the CH bond in the H_2COH group in 2,4-hexadien-1-ol under similar conditions even though both substances survived well in contact with strong aqueous base. The corresponding methyl ethers of the two alcohols also did not exchange, even after addition of dioxane to increase solubility in the water phase. Of course, the expected exchange sites on the alcohols and ethers were at saturated sp^3 carbon atoms rather than an sp^2 carbon atom, which is inherently more acidic. Table 1 includes one example of exchange at an sp^3 carbon, namely *cis*-3,4-dichlorobutene, where exchange occurred at the sp^3 carbon sites as well as at the sp^2 carbon atoms. Because the exchange at the sp^3 carbon atoms was slower, these CH bonds must be less acidic than the vinyl CH bond. Of course, the

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greater *s* character in the vinyl CH bond makes this bond more acidic.

Despite the qualitative character of the ranking of CH acidities in Table 1, it is possible to bracket the pK_a's by reference to known species. All of the weakly acidic CH bonds in Table 1 are significantly more acidic than ethylene (pK_a = 44)[1] and less acidic than acetylene (pK_a = 24).[1] Acetylene formed in the exchanges of 1-bromoethylene and 1-fluoroethylene exchanged quickly. In addition, Miller and Lee found 34 for the pK_a of *cis*-1,2-dibromoethylene in methanol.[5] Although the pK_a in methanol should be larger than in water, the value in water will not differ greatly. All considered, the species ranked in Table 1 should have pK_a's in the range of 40 to 30.

EXPERIMENTAL SECTION

Details of the conditions for the various exchange reactions can be found in the references given in Table 1. Here some general descriptions will suffice. All reactions were carried out in flame-sealed tubes. Of course, the attack of base on the glass lowers the base concentration over time. To slow the rate of attack of base on the reaction vessel in long exchanges, quartz tubes (with graded borosilicate seals) instead of borosilicate tubes were used. Mostly, the organic component was in the gas phase. Good contact between the gas phase and the water phase was maintained in a rocking oven.

When calcium oxide was used as the base, it had been baked at high temperature to remove the water that would degrade the isotopic purity of the D_2O. Calcium oxide was used in excess. Solutions of sodium deuteroxide were prepared from freshly cut and weighed sodium metal, which was put into D_2O in small pieces. Reaction vessels were rinsed with D_2O to ensure high deuterium content. Samples were prepared and worked up on a vacuum system with the organic component condensed on the frozen D_2O solutions at liquid nitrogen temperature. Careful freezing of the water prevented breaking the reaction vessel through formation of a solid plug of ice. The exchanged material was typically distilled from the D_2O solution at room temperature and then dried by distillation through a column containing phosphorus pentoxide. Repeated exchanges were used in most cases to obtain a high isotopic purity. The extent of exchange was assessed by gas-phase infrared spectra. Exchanges were done with isomeric mixtures unless otherwise indicated.

The calculations with the MP2 model with cc-pVTZ, cc-pVQZ, and aug-cc-pVQZ basis sets were carried with the Gaussian 03 and 09 software packages.[25] The tight convergence criterion was used throughout. For all ethylenes and related anions the input coordinates were in-plane Cartesians. All optimized ethylene structures were found to be planar even though planarity was not enforced. For the butadienes the input was expressed in internal coordinates, and planarity was enforced. The G03 calculations were performed on the Beowulf cluster at Oberlin College, and the G09 calculations were performed on the Ohio Supercomputer.

ASSOCIATED CONTENT

Supporting Information

Energies computed with the three QC models, MP2/cc-pVTZ, MP2/cc-pVQZ, and MP2/aug-cc-pVQZ, and energy differences for deprotonation and isomerization. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(30) The percent of *s* and *p* character for the bonds of the anion were computed at the MP2/cc-pVQZ level. G09 Rev C.01 failed to give this

output for the bonds of the anions when the basis set was expanded to aug-cc-pVQZ. As a test, comparison of the hybridizations computed with the cc-pVQZ and aug-cc-pVQZ basis sets for $H_2C{=}CFH$ gave differences of less than 0.04% for the *s* and *p* characters.

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