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An ab Initio Study of the Thermochemistry of Haloallenes

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Introduction

The need for reliable thermochemical data often outstrips the rate at which they can be generated from experiments. This is true even for some simple, fundamental molecules. For example, the thermochemical data for even the simplest of cumulenes, allenes, are scarce.[1] Since the enthalpies of formation have important applications in the studies of chemical reactivity and equilibrium, such values are very useful. We have recently used the combination of high level ab initio methods and isodesmic reaction schemes in order to obtain standard enthalpies of formation for haloethenes.[2] In this work we extend our investigations to haloallene derivatives. To obtain accurate enthalpies one needs to employ a computational method that provides sufficiently accurate total electronic energies. The newly introduced G3 method[3] was shown to provide such energies.[4] Also, accurate standard enthalpies for species participating in isodesmic reactions need to be known. As reference enthalpies, we have utilized the established enthalpies for ethene[5] and tetrafluoro-[6,7] and tetrachloroethene.[5] The standard experimental enthalpy for C_2F_4 is -658.56 ± 2.9 kJ/mol.[5] However, two recent theoretical studies[6,7] have suggested values of −671.5 and −668.6 kJ/mol, respectively. This implies that the experimental value is most probably incorrect. We have used the mean of the two theoretical results (−670.0 kJ/mol) as C_2F_4 enthalpy in this work.

Method of Calculation

The ab initio calculations were performed with Gaussian 98 program[8] which incorporates the G3 method as standard. The choice of "anchor" compounds in isodesmic reactions is important, so we have selected the compounds for which available experimental data are the most accurate and the most recent.[2,5] The reliability of the G3 method has been shown previously to be typically ±8.2 kJ/mol. The reason for not considering alternative methods of predicting enthalpies, based on atomization or formation reactions, is that such methods have been shown to be less accurate than suitable isodesmic reactions.[9] The molecular structures of haloallenes had been compared with experiment (where such data are available) and are shown in Table 1.

Table 1 indicates that the structural parameters are well reproduced by our calculations. The molecular structures parameters of the remaining haloallenes do not exhibit any significant trends. They vary within 10 pm/1° ranges and hence are not included in Table 1. It is also interesting that even small deviation of <CCC angle from 180° (allenes are slightly bent along CCC axis) is well reproduced by our calculations.

Results and Discussion

The results of the calculations are presented in Table 2. Table 2 displays ΔH_f^0 values for all the compounds studied together with the previous results for fluoroallenes[10] and the isodesmic reaction equations which were used in deducing enthalpies. The accurate enthalpy of propyne was taken from NIST-JANAF tables.[5] The enthalpy of parent allene was then derived from the isomerization reaction between propyne and allene. The enthalpies presented in Table 2 are useful because they enlarge the very small database of accurate thermochemical data on substituted cumulenes.[1] The discrepancies between previous[10] and present ΔH_f^0 values for fluoroallenes (Table 2) can be attributed to two factors: (1) an improved value for C_2F_4 enthalpy;[6,7] (2) the different levels of treating correlation energies in previous work[10] (MP2-valence) and current work (G3 method which includes QCISD).

The enthalpies of haloallenes in general become more negative and exothermic (i.e., the compounds become more stable thermodynamically) upon increasing the number of halogen substituents. However, this trend is more evident in fluoroallenes than in chloroallenes (Table 2). Besides enthalpy data themselves, it is interesting to deduce the influence of substituents on allene stability. In Table 3 we have presented a series of isodesmic reactions which permit us to determine relative stabilities of haloallenes vs haloethenes. The allene itself was found to be destabilized by 10.7 kJ mol^{-1} vs parent ethene.[1] The data in Table 3 indicate that chlorine and fluorine substitution leads to the destabilization of allene system ($\Delta H_r > 0$). The destabilization increases monotonically with increased halogenation. Fluoroallenes are destabilized more than their chloroallene counterparts by 13−24 kJ mol^{-1}. 1,1- and 1,3-Dihalo substitution patterns

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Table 1. Structural Parameters (Å, deg) for Haloallenes

molecule	calculated	experimental[11–13]
allene	CC = 1.311	1.3082
	CH = 1.080	1.076
	<HCH = 117.2	118.2
HFC_3H_2	CC = 1.309, 1.310	1.301, 1.309
	CF = 1.360	1.360
	CH = 1.080	1.086
	<CCC = 178.3	178.2
	<FCC = 122.3	121.9
	<HCC = 125.1, 121.6	124.3, 120.8
$F_2C_3H_2$	CC = 1.303, 1.310	1.306
	CF = 1.330	1.323
	<FCC = 124.9	124.9
$FClC_3H_2$	CC = 1.300, 1.310	1.301, 1.309
	CH = 1.080	1.086
	CF = 1.349	1.323
	CCl = 1.710	1.725
	<ClCC = 124.8	123.8
	<FCC = 122.9	122.5
	<HCH = 116.9	117.8

Table 2. ΔH_f^0 (g, 298.15 K)/kJmol^{-1} for Chlorofluoroallenes[a]

compound	previous[8]	this work	isodesmic reaction
allene	190.5[1]	188.0	$H_3CCCH \rightarrow H_2CCCH_2$ isomerization
C_3H_3F	29.7	22.4	$4C_3H_4 + C_2F_4 \rightarrow 4C_3H_3F + C_2H_4$
$F_2C_3H_2$	−147.7	−167.4	$2C_3H_4 + C_2F_4 \rightarrow 2F_2C_3H_2 + C_2H_4$
HFC_3HF	−134.3	−152.7	$2C_3H_4 + C_2F_4 \rightarrow 2HFC_3HF + C_2H_4$
C_3HF_3	−323.0	−348.8	$4C_3H_4 + 3C_2F_4 \rightarrow 4C_3HF_3 + 3C_2H_4$
C_3F_4	−518.0	−548.1	$C_3H_4 + C_2F_4 \rightarrow C_3F_4 + C_2H_4$
C_3H_3Cl		177.3	$4C_3H_4 + C_2Cl_4 \rightarrow 4C_3H_3Cl + C_2H_4$
$Cl_2C_3H_2$		167.6	$2C_3H_4 + C_2Cl_4 \rightarrow 2Cl_2C_3H_2 + C_2H_4$
$HClC_3HCl$		165.4	$2C_3H_4 + C_2Cl_4 \rightarrow 2HClC_3HCl + C_2H_4$
C_3HCl_3		154.6	$4C_3H_4 + {}_3C_2Cl_4 \rightarrow 4C_3HCl_3 + 3C_2H_4$
C_3Cl_4		142.5	$C_3H_4 + C_2Cl_4 \rightarrow C_3Cl_4 + C_2H_4$
$FClC_3H_2$		6.3	$4C_3H_4 + C_2Cl_4 + C_2F_4 \rightarrow 4FClC_3H_2 + 2C_2H_4$
HFC_3HCl		8.0	$4C_3H_4 + C_2Cl_4 + C_2F_4 \rightarrow 4HFC_3HCl + 2C_2H_4$
HFC_3Cl_2		−3.5	$4C_3H_4 + 2C_2Cl_4 + C_2F_4 \rightarrow 4HFC_3Cl_2 + 3C_2H_4$
$HClC_3FCl$		−8.8	$4C_3H_4 + 2C_2Cl_4 + C_2F_4 \rightarrow 4HClC_3FCl + 3C_2H_4$
$HClC_3F_2$		−184.5	$4C_3H_4 + C_2Cl_4 + 2C_2F_4 \rightarrow 4HClC_3F_2 + 3C_2H_4$
HFC_3FCl		−170.0	$4C_3H_4 + C_2Cl_4 + 2C_2F_4 \rightarrow 4HFC_3FCl + 3C_2H_4$
$FClC_3F_2$		−366.8	$4C_3H_4 + C_2Cl_4 + 3C_2F_4 \rightarrow 4FClC_3F_2 + 4C_2H_4$
$FClC_3Cl_2$		−21.3	$4C_3H_4 + 3C_2Cl_4 + C_2F_4 \rightarrow 4FClC_3Cl_2 + 4C_2H_4$
$F_2C_3Cl_2$		−197.5	$2C_3H_4 + C_2Cl_4 + C_2F_4 \rightarrow 2F_2C_3Cl_2 + 2C_2H_4$
$FClC_3FCl$		−188.2	$2C_3H_4 + C_2Cl_4 + C_2F_4 \rightarrow 2FClC_3FCl + 2C_2H_4$

[a] Appropriate haloethene isomers were used in isodesmic reactions; the superscripts indicate references.

Table 3. Relative Stabilities ΔH_r (kJ/mol) of Haloallenes vs Haloethenes

compound	ΔH_r	reaction
C_3H_4	10.7	$2C_2H_4 \rightarrow C_3H_4 + CH_4$
HFC_3H_2	36.2	$HFC{=}CH_2 + C_2H_4 \rightarrow HFC_3H_2 + CH_4$
$F_2C_3H_2$	53.7	$F_2C{=}CH_2 + C_2H_4 \rightarrow F_2C_3H_2 + CH_4$
HFC_3HF	54.7	$2HFC{=}CH_2 \rightarrow HFC_3HF + CH_4$
C_3HF_3	65.9	$F_2C{=}CH_2 + HFC{=}CH_2 \rightarrow C_3HF_3 + CH_4$
C_3F_4	73.9	$2F_2C{=}CH_2 \rightarrow C_3F_4 + CH_4$
$HClC_3H_2$	23.6	$HClC{=}CH_2 + C_2H_4 \rightarrow HClC_3H_2 + CH_4$
$Cl_2C_3H_2$	31.3	$Cl_2C{=}CH_2 + C_2H_4 \rightarrow Cl_2C_3H_2 + CH_4$
$HClC_3HCl$	37.7	$2\ HClC{=}CH_2 \rightarrow HClC_3HCl + CH_4$
C_3HCl_3	44.3	$Cl_2C{=}CH_2 + HClC{=}CH_2 \rightarrow C_3HCl_3 + CH_4$
C_3Cl_4	49.6	$2Cl_2C{=}CH_2 \rightarrow C_3Cl_4 + CH_4$
HFC_3HCl	47.9	$HFC{=}CH_2 + HClC{=}CH_2 \rightarrow HFC_3HCl + CH_4$
$FClC_3H_2$	42.5	$FClC{=}CH_2 + C_2H_4 \rightarrow FClC_3H_2 + CH_4$
F_2C_3HCl	62.7	$F_2C{=}CH_2 + HClC{=}CH_2 \rightarrow F_2C_3HCl + CH_4$
$FClC_3HF$	59.7	$FClC{=}CH_2 + HFC{=}CH_2 \rightarrow FClC_3HF + CH_4$
Cl_2C_3HF	53.7	$Cl_2C{=}CH_2 + HFC{=}CH_2 \rightarrow Cl_2C_3HF + CH_4$
$ClFC_3HCl$	53.4	$ClFC{=}CH_2 + HClC{=}CH_2 \rightarrow ClFC_3HCl + CH_4$
$F_2C_3Cl_2$	67.1	$F_2C{=}CH_2 + Cl_2C{=}CH_2 \rightarrow F_2C_3Cl_2 + CH_4$
$FClC_3FCl$	64.0	$2\ FClC{=}CH_2 \rightarrow FClC_3FCl + CH_4$
F_2C_3FCl	70.3	$F_2C{=}CH_2 + FClC{=}CH_2 \rightarrow F_2C_3FCl + CH_4$
Cl_2C_3FCl	58.3	$Cl_2C{=}CH_2 + FClC{=}CH_2 \rightarrow Cl_2C_3FCl + CH_4$

Table 4. Mulliken Population Analysis for Haloallenes at MP2/6-31G* Level. The Numbers Represent Partial Atomic Charges. X = F or Cl

compound	X	C	C	C	X
allene		−0.505	0.208	−0.505	
HFC_3H_2	−0.372	0.118	0.086	−0.455	
$F_2C_3H_2$	−0.339	0.647	0.016	−0.418	
HFC_3FH	−0.360	0.168	−0.042	0.168	−0.360
HFC_3F_2	−0.354	0.207	−0.112	0.693	−0.327
C_3F_4	−0.321	0.735	−0.185	0.735	−0.321
$HClC_3H_2$	−0.016	−0.425	0.235	−0.472	
$Cl_2C_3H_2$	0.058	−0.378	0.270	−0.455	
$HClC_3ClH$	−0.008	−0.399	0.263	−0.399	−0.008
$HClC_3Cl_2$	0.023	−0.398	0.301	−0.361	−0.079
C_3Cl_4	0.092	−0.355	0.342	−0.355	0.092

Table 5. Relative Stabilities (kJ/mol) of 1,1- vs 1,3-Haloallenes

compound	1,3-isomer
$C_3H_2F_2$	14.8
$C_3H_2Cl_2$	−2.2
C_3H_2FCl	1.8
C_3HFCl_2	−5.3
C_3HF_2Cl	14.4
$C_3F_2Cl_2$	9.3

(isomers) show little difference in stability; the difference falls within uncertainty range of G3 method (N.B. the average uncertainty for the G3 method is ±8.2 kJ mol^{-1}). This can be expected in view of the nonconjugated nature of allenic π-bonds and is at variance with haloethenes where distinct differences in stability between 1,1- and 1,2-substituted haloethenes were observed.[2]

To gain better insight into these variations of thermodynamic stability we have performed population analysis. The results are presented in Table 4. In fluoroallenes, the increased halogenation leads to the increased negative charge on central carbon while no effect of comparable magnitude appears in chloroallenes. One can tentatively suggest that increasing CC bond polarization plays a part in destabilizing fluoroallenes, but that in chloroallenes it has little significance. Table 5 describes relative stabilities of 1,1- vs 1,3-haloallene isomers. The results displayed can be compared with relative isomer stabilities of corresponding haloethenes. For the range of compounds studied, 1,1-isomers appear to be more stable than 1,3- with two exceptions. The exceptions are however within the uncertainty limits of the G3 method. The similar effect, i.e., enhanced stability of 1,1- over 1,2-isomers, was observed in haloethenes[2] although there the effect was more pronounced. The enhanced stability of 1,1- over 1,3- isomers can be attributed to the preponderance of LP (lone pair) interactions between halogen lone pair and σ antibonding orbitals along the lines of the same argument as presented earlier.[2] Among two other types of possible interactions, geminal interactions are known to be small,[2] while vicinal interactions in allenes are quenched due to molecular symmetry.

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