

## Chlorofluoroethenes. Thermochemical Stability and Cis-Effect

Igor Novak

Department of Chemistry, National University of Singapore,  
Singapore 117543, Singapore

chmigorn@nus.edu.sg

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### Introduction

The need for reliable thermochemical data often outstrips the rate at which they can be generated from experiments.<sup>1</sup> For example, enthalpies of formation have important applications in studies of chemical reactivity and equilibrium, but precise enthalpy values are known for only a small number of tetra- and penta-atomic molecules.<sup>2</sup> We have used a combination of high level ab initio methods and isodesmic reaction<sup>3</sup> schemes to obtain standard enthalpies of formation. In this way we hope to fill the gaps in our knowledge of enthalpies and also to analyze trends in thermochemical stability along series of related compounds. To obtain accurate enthalpies one needs to employ a computational method that provides sufficiently accurate total electronic energies (e.g., the newly introduced G3 method which was shown to provide such energies<sup>4</sup>). Also, accurate standard enthalpies for species participating in isodesmic reactions need to be known. As reference enthalpies, we have utilized experimental enthalpies for ethane, tetrafluoroethene and tetrachloroethene.

### Method of Calculation

The ab initio calculations were performed with Gaussian 98 set of programs<sup>5</sup> which incorporates G3 method as a standard. The choice of “anchor” compounds in isodesmic reactions is not

Table 2. Relative Stabilities of Isomers (kJ/mol)

compd	[1,1]	cis	trans
C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	0.0	41.54	44.42
C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	0.0	-0.97	1.54
C <sub>2</sub> H <sub>2</sub> FCl	0.0	11.6	14.5
C <sub>2</sub> HF <sub>2</sub> Cl	0.0	25.5	25.0
C <sub>2</sub> HFCl <sub>2</sub>	0.0	-8.6	-9.0
C <sub>2</sub> F <sub>2</sub> Cl <sub>2</sub>	0.0	15.9	13.9

unique so we have selected the compounds for which the available experimental data are the most accurate and most recent.<sup>2,6,7</sup> The reliability of G3 method has been shown to be  $\pm 8.2$  kJ/mol.<sup>7</sup> Natural bond orbital analysis (NBO) had been performed at MP2(full)/6-61 g(d,p) level. 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.<sup>8,9</sup>

### Results and Discussion

The results of the calculations are presented in Tables 1–3. Table 1 displays values for the three “anchor” compounds together with isodesmic reaction equations which were used in deducing enthalpies for each compound. The enthalpies derived experimentally are often obtained through a variety of methods each of them having different accuracy. Table 1 provides an essential guide for the experimentalist about the reliability or the need for revision of certain values. For example, the enthalpies for dichloroethenes and trichloroethenes should be remeasured (Table 1). Trichloroethene is a case in point. Although values from NIST and Gurvich compilations agree well, it is so only because they use the same primary source.

In general, the enthalpies become more negative and exothermic (i.e. the compounds become more stable thermodynamically) upon increasing the number of halogen substituents. However, a more interesting trend concerns relative stability of 1,1-, cis and trans isomers (Table 2). Two observations deserve explicit comment.

Table 1.  $\Delta H_f^\circ(\text{g}, 298.15\text{K})/\text{kJmol}^{-1}$  for Chlorofluoroethenes

compd	Gurvich <sup>2</sup>	NIST <sup>6</sup>	ab initio	isodesmic reaction
C <sub>2</sub> H <sub>4</sub>		52.467		
C <sub>2</sub> F <sub>4</sub>			-671.57	
C <sub>2</sub> Cl <sub>4</sub>		-12.426		
C <sub>2</sub> H <sub>3</sub> F	-140.1	-136.0	-141.5	3C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> F <sub>4</sub> = 4C <sub>2</sub> H <sub>3</sub> F
[1,1] C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	-336.4	-334	-349.2	C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> F <sub>4</sub> = 2C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>
cis-C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	-313.2		-307.7	C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> F <sub>4</sub> = 2C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>
trans-C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	-310.0		-304.8	C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> F <sub>4</sub> = 2C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>
C <sub>2</sub> H <sub>3</sub> Cl	23.0	29.0	26.4	3C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> Cl <sub>4</sub> = 4C <sub>2</sub> H <sub>3</sub> Cl
[1,1] C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	2.3	2.2	9.0	C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> Cl <sub>4</sub> = 2C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>
cis-C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	4.1	4.3	8.0	C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> Cl <sub>4</sub> = 2C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>
trans-C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	6.1	1.7	10.6	C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> Cl <sub>4</sub> = 2C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>
C <sub>2</sub> HF <sub>3</sub>	-491.0	-474.0	-496.5	C <sub>2</sub> H <sub>4</sub> + 3C <sub>2</sub> F <sub>4</sub> = 4C <sub>2</sub> HF <sub>3</sub>
C <sub>2</sub> HCl <sub>3</sub>	-19.1	-19.1	-4.2	C <sub>2</sub> H <sub>4</sub> + 3C <sub>2</sub> Cl <sub>4</sub> = 4C <sub>2</sub> HCl <sub>3</sub>
[1,1]C <sub>2</sub> H <sub>2</sub> FCl	-165.4		-163.9	2C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> F <sub>4</sub> + C <sub>2</sub> Cl <sub>4</sub> = 4C <sub>2</sub> H <sub>2</sub> FCl
cis-C <sub>2</sub> H <sub>2</sub> FCl	-155.4		-152.3	2C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> F <sub>4</sub> + C <sub>2</sub> Cl <sub>4</sub> = 4C <sub>2</sub> H <sub>2</sub> FCl
trans-C <sub>2</sub> H <sub>2</sub> FCl	-152.4		-149.4	2C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> F <sub>4</sub> + C <sub>2</sub> Cl <sub>4</sub> = 4C <sub>2</sub> H <sub>2</sub> FCl
[1,1]C <sub>2</sub> HF <sub>2</sub> Cl	-334.0		-347.4	C <sub>2</sub> H <sub>4</sub> + 2C <sub>2</sub> F <sub>4</sub> + C <sub>2</sub> Cl <sub>4</sub> = 4C <sub>2</sub> HF <sub>2</sub> Cl
cis-C <sub>2</sub> HF <sub>2</sub> Cl	-323.6		-321.9	C <sub>2</sub> H <sub>4</sub> + 2C <sub>2</sub> F <sub>4</sub> + C <sub>2</sub> Cl <sub>4</sub> = 4C <sub>2</sub> HF <sub>2</sub> Cl
trans-C <sub>2</sub> HF <sub>2</sub> Cl	-323.1		-322.5	C <sub>2</sub> H <sub>4</sub> + 2C <sub>2</sub> F <sub>4</sub> + C <sub>2</sub> Cl <sub>4</sub> = 4C <sub>2</sub> HF <sub>2</sub> Cl
[1,1]C <sub>2</sub> HFCl <sub>2</sub>	-159.1		-160.7	C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> F <sub>4</sub> + 2C <sub>2</sub> Cl <sub>4</sub> = 4C <sub>2</sub> HFCl <sub>2</sub>
cis-C <sub>2</sub> HFCl <sub>2</sub>	-168.2		-169.3	C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> F <sub>4</sub> + 2C <sub>2</sub> Cl <sub>4</sub> = 4C <sub>2</sub> HFCl <sub>2</sub>
trans-C <sub>2</sub> HFCl <sub>2</sub>	-169.1		-169.7	C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> F <sub>4</sub> + 2C <sub>2</sub> Cl <sub>4</sub> = 4C <sub>2</sub> HFCl <sub>2</sub>
[1,1]C <sub>2</sub> F <sub>2</sub> Cl <sub>2</sub>	-338.0		-348.8	C <sub>2</sub> F <sub>4</sub> + C <sub>2</sub> Cl <sub>4</sub> = 2C <sub>2</sub> F <sub>2</sub> Cl <sub>2</sub>
cis-C <sub>2</sub> F <sub>2</sub> Cl <sub>2</sub>	-325.2		-332.9	C <sub>2</sub> F <sub>4</sub> + C <sub>2</sub> Cl <sub>4</sub> = 2C <sub>2</sub> F <sub>2</sub> Cl <sub>2</sub>
trans-C <sub>2</sub> F <sub>2</sub> Cl <sub>2</sub>	-324.1		-334.9	C <sub>2</sub> F <sub>4</sub> + C <sub>2</sub> Cl <sub>4</sub> = 2C <sub>2</sub> F <sub>2</sub> Cl <sub>2</sub>
C <sub>2</sub> F <sub>3</sub> Cl	-515.2	-505.5	-504.4	3C <sub>2</sub> F <sub>4</sub> + C <sub>2</sub> Cl <sub>4</sub> = 4 C <sub>2</sub> F <sub>3</sub> Cl
C <sub>2</sub> FCl <sub>3</sub>	-166.0		-175.2	C <sub>2</sub> F <sub>4</sub> + 3C <sub>2</sub> Cl <sub>4</sub> = 4C <sub>2</sub> FCl <sub>3</sub>

**Table 3. NBO Analysis for Chlorofluoroethenes. the Numbers Represent Delocalization/Stabilization Energies (kcal/mol) Due to Particular Types of Interactions<sup>a</sup>**

molecule	geminal	vicinal (P & AP)	LP
[1,1]C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	5.24 (3.7)	24.86 (17.6)	109.18 (77.4)
<i>cis</i> -C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	4.12 (3.9)	18.48 (17.4)	83.32 (78.7)
<i>trans</i> -C <sub>2</sub> H <sub>2</sub> F <sub>2</sub>	4.42 (4.4)	18.28 (18.0)	78.98 (77.6)
[1,1] C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	5.42 (5.5)	20.16 (20.0)	74.94 (74.5)
<i>cis</i> -C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	0	24.18 (24.5)	74.68(75.5)
<i>trans</i> -C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	0	21.28 (24.0)	67.46 (76.0)
[1,1]C <sub>2</sub> H <sub>2</sub> FCl	2.71 (2.3)	26.84 (22.3)	90.7 (75.4)
<i>cis</i> -C <sub>2</sub> H <sub>2</sub> FCl	2.45 (2.4)	21.4 (20.8)	79.0 (76.8)
<i>trans</i> -C <sub>2</sub> H <sub>2</sub> FCl	2.37 (2.5)	18.28 (19.3)	73.92 (78.2)
[1,1]C <sub>2</sub> HF <sub>2</sub> Cl	2.22 (1.3)	19.97 (12.0)	144.9 (86.7)
<i>cis</i> -C <sub>2</sub> HF <sub>2</sub> Cl	3.62 (2.4)	16.89 (11.1)	131.3 (86.5)
<i>trans</i> -C <sub>2</sub> HF <sub>2</sub> Cl	3.77 (2.5)	17.34 (11.3)	132.3 (86.3)
[1,1]C <sub>2</sub> HFCl <sub>2</sub>	2.1 (1.5)	18.91 (13.4)	119.95 (85.1)
<i>cis</i> -C <sub>2</sub> HFCl <sub>2</sub>	2.14 (1.4)	22.37 (14.5)	130 (84.1)
<i>trans</i> -C <sub>2</sub> HFCl <sub>2</sub>	2.24 (1.5)	19.64 (13.0)	128.6 (85.5)
[1,1]C <sub>2</sub> F <sub>2</sub> Cl <sub>2</sub>	3.86 (1.8)	16.64 (8.0)	188.3 (90.2)
<i>cis</i> C <sub>2</sub> F <sub>2</sub> Cl <sub>2</sub>	3.24 (1.6)	14.44 (7.1)	184.4 (91.3)
<i>trans</i> -C <sub>2</sub> F <sub>2</sub> Cl <sub>2</sub>	3.34 (2.2)	15.66 (10.3)	133.3 (87.5)

<sup>a</sup> The number in brackets represents percent of total delocalization energy.

The first observation concerns dichloroethenes. The compilation published by Gurvich et al.<sup>2</sup> suggests that 1,1- is the most stable among C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub> isomers, while G3 method predicts highest stability for the *cis* isomer. However, since the discrepancy is <2 kJ/mol (i.e., within G3 uncertainty) the argument remains inconclusive. The second point of interest is that 1,1-isomer is the most stable one except in C<sub>2</sub>HFCl<sub>2</sub>. The reduction in stability of 1,1-isomers of C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub> and C<sub>2</sub>HFCl<sub>2</sub> can at first glance be attributed to the interactions between geminal chlorine atoms. To gain greater insight into the causes of these variations in thermodynamic stability we have performed NBO analysis.

Enhanced relative thermodynamic stability of *cis* vs *trans* isomer has been a long-standing problem in organic chemistry for which a variety of explanations had been offered.<sup>10</sup> In this work we have analyzed the relative stability of all 3 possible isomers: 1,1-, *cis* and *trans*. Our approach is similar to Yamamoto and Tomoda's work,<sup>10</sup> i.e., we rely on 2nd order perturbation analysis of natural bonding orbitals to identify major factors influencing contributions to orbital (de)stabilization. However, unlike previous work, we have considered all possible interactions between localized bonding, nonbonding and antibonding orbitals i.e., vicinal (both periplanar and anti-periplanar), lone pair (LP) and geminal interactions (Table 3).

The geminal interactions considered include  $\sigma_{CH} \rightarrow \sigma_{CX}^*$  and  $\sigma_{CX} \rightarrow \sigma_{CY}^*$ ; they amount to 2–5% of total stabiliza-

tion energy and their importance decreases with increasing halogenation.

The vicinal interactions considered ( $\sigma_{CX} \rightarrow \sigma_{CY}^*$ ,  $\sigma_{CH} \rightarrow \sigma_{CX}^*$ ,  $\sigma_{CX} \rightarrow \sigma_{CH}^*$ ) which can be periplanar (P) or anti-periplanar (AP) are of greater importance than geminal ones. They amount to 8–24% of stabilization energy and they decrease with increasing degree of halogenation.

Lone pair (LP) interactions considered here ( $n_o^X \rightarrow \sigma_{CX}^*$ ,  $n_o^X \rightarrow \sigma_{CH}^*$ ,  $n_o^X \rightarrow \sigma_{CC}^*$ ,  $n_r^X \rightarrow \pi_{CC}^*$ ) are the most important and increase with increasing degree of halogenation. For example, Table 3 shows that LP effects in 1,1-dichloro-2-fluoroethene (C<sub>2</sub>HFCl<sub>2</sub>) isomer are smaller than in either *cis* or *trans* which explains its reduced stability vs the other two isomers. However, one cannot simply attribute the destabilization of 1,1-isomer to geminal effects of two large chlorine atoms. If this were the proper rationalization than why is 1,1-isomer of C<sub>2</sub>F<sub>2</sub>-Cl<sub>2</sub> more stable than either *cis* or *trans*? In fact the  $n_o^X \rightarrow \sigma_{CX}^*$  interactions in 1,1-dichloro-2-fluoroethene (C<sub>2</sub>-HFCl<sub>2</sub>) are smaller (24.87 kcal/mol) than in either *cis* or *trans* isomers (31.5 and 31.3 kcal/mol, respectively). The caveat is that all possible interactions must be considered before a plausible rationale for thermodynamic stability can be arrived at.

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