

Property Estimation of Halons
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ABSTRACT

Only a small fraction of the possible halon alternatives has an adequate set of experimentally determined physical and chemical data. For the remainder it is necessary to estimate the relevant values. Many of the properties that are needed to evaluate a compound for fire suppression effectiveness, ozone depletion potential, greenhouse effect and materials compatibility can be currently estimated with acceptable accuracy. The properties for which estimation techniques are inadequate are atmospheric chemical reactivity, infra-red spectral absorbance and heat of formation. Techniques are presented here to produce better estimates for heats of formation.

The most widely used approximation techniques are based on the idea of group additivity. These methods rely on evaluating a property of the molecule by adding up contributions based on individual multivalent atoms. These techniques are well established for the prediction of thermochemical properties (ΔH_f , S , C_p) and have been extended in a limited way to estimation of rates of reaction for OH. The group values for thermochemical properties have been established for most of the simple organic compounds; however, the data for the halogenated compounds, and especially the highly fluorinated compounds are not as well established.

In order to improve the accuracy of the group values for predicting heat of formation of halogenated compounds, the currently available thermochemical data on the saturated halocarbons have been reexamined with emphasis on the highly fluorinated compounds. These compounds, while very stable, are less stable than would be predicted from based on data derived from less highly fluorinated molecules, in many cases the error in predicted stability is 70 to 80 kJ/mol for small molecules (C, species) and increase with molecular size. To correct this it was necessary to add a new type of central carbon atom to the group definitions - a C_f which is defined as a carbon atom with two or more fluorines attached to it. Using this central atom, it was possible to establish a set of groups that would allow the prediction of all of the heats of formation of the halocarbons. Even so, the accuracy of the prediction is less than would be expected from data for molecules that do not contain fluorine.

INTRODUCTION

The approximation techniques that have proved to be the most useful in estimating physical and thermochemical properties of molecules all rely on some form of simple additivity. That is the property of the molecule is expressed as a linear sum of values associated with atoms within the molecule:

$$P_m = \sum P_i$$

where the sum will run over an appropriate set of atoms for the approximation technique

We can categorize these linear approximation techniques by orders that are depend on how the p_i are chosen. The first order approximations use only the identity of the atom, for example the molecular weight, where the p_i are the atomic weights of the individual atoms. In many cases it is necessary to extend the first order technique to take into account the valence state of the atom in question, Joback's method (87REI/PRA) for normal boiling points falls into this category of approximation. For more exact approximation it is necessary to move to second order techniques. Here the p_i are associated not with just the atom, or the atom and its valence state, but the atom and its nearest neighbors. In the case of the most widely used technique of this type - the Benson group method (76BEN) - the sum over p_i runs over the multivalent atoms in the molecule. For example 1,1,1 trifluoroethane would have two distinct multivalent atoms - both carbon; one attached to three fluorines and a carbon, one attached to three hydrogens and a carbon. There are two groups to contribute to the molecule, one associated with each of the carbon atoms. The group values are built up by using data for molecules that have limited numbers of groups and solving for the values of the groups. For example ethane has 2 C-H₃C groups, that is a carbon atom attached to 3 hydrogens and an additional carbon. Since there are no other contributions to the heat of formation of ethane the group value for the heat of formation for C-H₃C is just one half the heat of formation of ethane. In the same way propane has two C-H₃C groups and one C-H₂C₂ group. Thus using propane and ethane the value of two groups can be determined. This can be made more systematic by not using just a single heat of formation for each group but by determining the group values in a manner that will provide the smallest absolute error for a large data set. There are other factors considered in the complete group additivity model which are longer range interactions, for example - ring strain, cis-trans isomers, gauche interactions or ortho, meta, para substitutions on aromatic rings.

APPLICATION TO HALONS

Like all linear approximation techniques, it is necessary to have a data set from which to extract the parameters for the model, and in the case of the halons the resulting data requirements are large. To illustrate the size of the problem it is useful to compare the hydrocarbon primary carbon atom - the C-H₃C discussed above, to the number of groups needed for the primary carbons for all of the halons. These groups are designated by the central atom, followed by the attached atoms. For the halons the groups needed are C-H₂FC, C-HF₂C, C-F₃C, C-F₂ClC, C-FCl₂C, C-Cl₃C, etc. for a total of 19 distinct groups just for the primary carbon attached to a saturated carbon with H,F,Cl, or Br attached to it. While for some applications, it may be possible to use data for C-F₃C, C-F₂BrC, and C-Br₃C to predict C-FBr₂C, for the best accuracy it is necessary to derive the value of these groups from thermochemical data. The problem is more complex for the highly fluorinated halons. Fluorine substitution, unlike the other halogen atoms, is increasingly stable as more fluorines are substituted on a carbon atom - see Table 1 (86SMA). However, this additional stability is less pronounced in perfluorinated compounds. So that if one were to predict a group value for C-F₃C from data for 1,1,1-trifluoroethane, and apply it to the prediction of perfluoroethane, the result would be over predict the stability of perfluoroethane relative to the measured heat of formation by 68 kJ/mol. This property of the highly fluorinated compounds is well known and can be illustrated by the changes in C-C bond energy as ethane is fluorinated. It is possible to take these effects into

account within the framework of the group additivity method. To do this the same general technique is used as to account for other variations of the central carbon atom.

Table 1: Molecular properties of fluorometanes

Compound	C-F Bond Length (nm)	C-F Bond Energy (kJ/mol)
CH ₃ F	0.1385	474.1
CH ₂ F ₂	0.1357	515.5
CHF ₃	0.1332	550.0
CF ₄	0.1319	563

The group additivity method has a number of different types of carbon - C (saturated carbon), C_d (doubly bonded), C_t (triply bonded), C_b (aromatic carbon), C_{bf} (fused ring aromatic) - these represent not only different valence states, but also different electronic environments which correspond to different energies. In the same way we may define a C_f to be a carbon atom with at least *two* fluorines bonded to it. For most situations the C_f has the same value as a saturated carbon with the same constituents, the exception to this rule is when C_f is bonded to another C_f. Using this as an analysis tool a set of groups that will be useful in estimating the heats of formation of halons was derived from the available literature data. The data analyzed included 72 compounds from which group values for 39 groups were extracted. The compounds, thermochemical data, and reference are given in Table 2. The values for the resultant groups are given in Table 3 as is the number of such groups in the data set. Data for other groups used in the analysis are also included in Table 3. For many of the groups, there are no data but the groups are included in the table for completeness. Subsequent analysis of the groups for which there is data and the changes in bond energy with halon substitution may allow for at least approximate values of these groups to be provided.

Note that the simple discussion of the difference between perfluoroethane and 1,1,1-trifluoroethane a difference of 68 kJ/mol was indicated. The groups shown in Table 3 would only provide a 16 kJ/mol difference between the two calculations. This reflects the results of taking not only the data for these two molecules, but also the data for the entire set given in Table 2. The results of the current set of group values gives calculated values for the perfluoroethane that is 24 kJ/mol too stable and 12 kJ/mol less stable for the 1,1,1-trifluoroethane than the experimental data. The most dramatic differences between the fluorinated and the normal carbons are seen in the values associated with the secondary carbon atoms. Here there are three fluorocarbon groups that replace the C-H₂C₂ group, C-F₂C_f, C-F₂C_fC, C-F₂C₂ with group values of -405, -439, -460 kJ/mol respectively. This set of groups shows the effect of increasing fluorine substitution on the adjacent carbon atoms most directly.

It is important to note that as with any set of parameters derived from data, the parameters are only as good as the underlying data. Thermochemical measurements on halocarbons are much more difficult than the same measurements on hydrocarbons and there is simply not as large a data

set to provide for adequate cross checking. The data set included in this paper is maintained in a spread sheet format to allow for rapid recalculation of the relevant group values as more data become available. In addition allowance has been made for dealing in a consistent fashion with data that appears to be strongly at odds with the rest of the data set (see footnote to Table 2). The advantage of using this set of parameters over those that do not allow for the effect of the highly fluorinated carbon interactions is that very large errors will in general be avoided. Without the C_f group the possibility for such errors is much greater.

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TABLE 2: THERMOCHEMICAL DATA USED IN ESTABLISHING HALOCARBON GROUPS - VALUES IN KJ/MOL

	Compound	Measured	Calculated	Errors	Reference	Corrections
1	C ₂ F ₆	-1344.0	-1368.2	-24.2	83KOL/PAP	
2	C ₃ F ₈	-1784.0	-1772.8	11.2	86KOL/KOZ	
3	n-C ₇ F ₁₆	-3385.0	-3391.1	-6.1	86KOL/KOZ	
4	CH ₃ CHFCH ₃	-286.2	-269.4	16.8	86KOL/KOZ	
5	CH ₃ CH ₂ CH ₂ F	-279.1	-285.1	-6.0	86KOL/KOZ	
6	CF ₃ CH ₂ CF ₃	-1406.1	-1401.3	4.8	86KOL/KOZ	
7	CF ₃ CH ₂ CH ₂ Cl	-779.7	-777.9	1.8	86KOL/KOZ	
8	CF ₃ CH ₂ CCl ₃	-803.9	-798.9	5.0	86KOL/KOZ	2-g-CF ₃ -Cl
9	CF ₃ CH ₂ CHCl ₂	-791.3	-794.7	-3.4	86KOL/KOZ	1-g-CF ₃ -Cl
10	CH ₃ CH ₂ CH ₂ Cl	-132.5	-130.2	2.3	86KOL/KOZ	
11	CF ₃ CH ₂ CFCl ₂	-970.3	-970.4	-0.1	86KOL/KOZ	1-g-CF ₃ -Cl
12	CF ₃ CH ₂ CH ₂ OH	-921.0	-903.5	17.5	86KOL/KOZ	
13	CF ₃ CF ₂ CH ₂ OH	-1309.1	-1315.9	6.8	86KOL/KOZ	
14	CF ₂ HCF ₂ CH ₂ OH	-1064.8	-1075.3	-10.5	86KOL/KOZ	
15	CF ₃ (CF ₂) ₂ CH ₂ OH	-1739.7	-1720.5	19.2	86KOL/KOZ	
16	(CF ₃ CH ₂ CH ₂) ₂ O	-1604.4	-1586.8	17.6	86KOL/KOZ	
17	(C ₃ F ₇) ₂ O	-3148.2	-3169.8	-21.6	86KOL/KOZ	
18	(C ₄ F ₉) ₂ O	-3979.2	-3979.0	0.2	86KOL/KOZ	
19	(C ₅ F ₁₁) ₂ O	-4806.4	-4788.2	18.2	86KOL/KOZ	
20	CFCl ₂ CF ₂ OCCl ₃	-901.2	-900.4	0.8	86KOL/KOZ	
21	CF ₃ CH ₂ CF ₂ Cl	-1151.5	-1179.6	-28.1	86KOL/KOZ	
22	CF ₂ ClCFCl ₂	-726.8	-719.6	7.2	83KOL/PAP	1-g-Cl-Cl
23	CH ₃ CF ₂ Cl	-536.2	-511.3	24.9	83KOL/PAP	
24	CFClHCF ₂ OCH ₃	-882.3	-867.8	14.5	86KOL/KOZ	
25	CFClHCF ₂ OCH ₂ CF ₂ CF ₂ H	-1720.7	-1741.8	-21.1	86KOL/KOZ	
26	CFClHCF ₂ OCH ₂ (CF ₂) ₃ CF ₂ H	-2555.6	-2551.0	4.6	86KOL/KOZ	
27	CFClHCF ₂ OCH ₂ (CF ₂) ₅ CF ₂ H	-3391.9	-3360.2	31.7	86KOL/KOZ	
26	CF ₃ CF ₂ COOCH ₃	-1428.3	-14347	6.4	86KOL/KOZ	
29	CF ₃ (CF ₂) ₂ COOCH ₃	-1843.0	-1839.3	3.7	86KOL/KOZ	
30	CF ₃ CFHCF ₂ OCH ₂ CF ₂ CF ₂ H	-2359.0	-2356.8	2.2	86KOL/KOZ	
31	CF ₃ CFHCF ₂ OCH ₂ (CF ₂) ₃ CF ₂ H	-3162.4	-3179.8	-17.4	86KOL/KOZ	
32	CH ₂ OH-(CF ₂) ₄ -CH ₂ OH	-2084.2	-2072.8	11.4	86KOL/KOZ	
33	cyclo-C ₆ F ₁₄	-2370.4	-2419.2	-48.8	86PED/NAY	r-6
34	cyclo-C ₆ F ₁₁ CF ₃	-2897.2	-2899.5	-2.3	86PED/NAY	r-6
35	cyclo-C ₆ F ₁₁ C ₂ F ₅	-3302.1	-3304.1	-2.0	86PED/NAY	r-6
36	(CF ₃) ₂ CF(CF ₂) ₄ CF(CF ₃) ₂	-4639.1	-4756.4	-117.3	89ZHO/PAP	
37	CH ₃ CF ₃	-744.6	-733.0	11.6	86PED/NAY	
38	CH ₃ CHF ₂	-497.0	-502.9	-5.9	83KOL/PAP	
39	CH ₂ FCHF ₂	-691.0	-682.0	9.0	83KOL/PAP	
40	CH ₃ CH ₂ Cl	-112.2	-109.6	2.6	83KOL/PAP	

TABLE 2: THERMOCHEMICAL DATA USED IN ESTABLISHING HALOCARBON GROUPS - VALUES IN KJ/MOL

	Compound	Measured	Calculated	Errors	Reference	Corrections
41	CH ₃ CHCl ₂	-130.6	-130.5	0.1	83KOL/PAP	
42	CH ₃ CCl ₃	-144.6	-138.9	5.7	83KOL/PAP	
43	CH ₂ CICHCl ₂	-144.7	-142.3	2.4	83KOL/PAP	1-g-Cl-Cl
44	CH ₂ CICCl ₃	-152.3	-159.0	6.7	83KOL/PAP	2-g-Cl-Cl
45	CH ₃ CHFCI	-313.4	-323.0	-9.6	83KOL/PAP	
46	perfluoro <i>trans</i> -decalin	-3644.5	-3642.6	1.9	87ZHO/PAP	r-t[4.4.0]
47	perfluoro <i>cis</i> -decalin	-3624.1	-3621.7	2.4	87ZHO/PAP	r-c[4.4.0]
48	perfluoro <i>cis</i> -bi[4.3.0]nonane	-3212.2	-3212.9	0.7	88ZHO/PAP2	r-c[4.3.0]
49	CHCl ₂ CHCl ₂	-157.3	-150.6	6.7	83KOL/PAP	2-g-Cl-Cl
50	CH ₃ CH ₂ Br	61.5	-59.4	2.1	83KOL/PAP	
51	CH ₃ CHBr ₂	-26.7	-25.9	0.8	83KOL/PAP	
52	CH ₂ BrCH ₂ Br	-38.3	-33.5	4.8	83KOL/PAP	
53	CF ₂ BrCF ₂ Br	-789.9	-786.6	3.3	83KOL/PAP	
54	CH ₃ CF ₂ Br	474.3	444.3	30.0	83KOL/PAP	
55	CF ₃ CH ₂ Br	697.8	-707.1	-9.3	83KOL/PAP	
56	CHF ₂ CF ₂ Br	-833.2	-836.8	-3.6	83KOL/PAP	
57	CF ₂ CICF ₂ Cl	-325.5	-928.8	-3.3	83KOL/PAP	
58	CF ₃ CFCICF ₂ Cl	-1324.7	-1322.1	2.6	86KOL/KOZ	1-g-Cl-Cl
59	CFCl ₂ CF ₂ OCF ₂ Cl	-1325.6	-1327.2	-1.6	86KOL/KOZ	
60	CFCl ₂ CF ₂ OCCl ₂ CF ₂ CF ₂ Cl	-1752.5	-1753.9	-1.4	86KOL/KOZ	
61	CFCl ₂ CF ₂ OCCl ₂ (CF ₂) ₃ CF ₂ Cl	-2560.6	-2563.1	-2.5	86KOL/KOZ	
62	CH ₃ CHClBr	-32.0	-72.0	10.0	83KOL/PAP	
63	CHClBrCHClBr	-36.0	-33.5	2.5	83KOL/PAP	
64	CF ₂ BrCFCIBr	616.8	-619.2	-2.4	83KOL/PAP	1-g-Cl-Br
65	CF ₃ CHClBr	-699.9	-719.6	-19.7	83KOL/PAP	
66	CF ₂ BrCHFCI	-654.7	-682.0	-27.3	83KOL/PAP	
67	CF ₂ BrCHCl ₂	471.0	477.0	6.0	83KOL/PAP	1-g-Br-Cl
68	CH ₃ CHClCH ₃	-144.9	-139.7	5.2	86PED/NAY	
69	CH ₃ CCl ₂ CH ₃	-173.2	-173.2	0.0	86PED/NAY	
70	CH ₂ CICH ₂ CH ₂ Cl	-159.2	-154.5	4.7	86PED/NAY	
71	CH ₂ CICHClCH ₃	-162.8	-164.0	-1.2	86PED/NAY	
72	CH ₂ CICHClCH ₂ Cl	-182.9	-188.3	-5.4	86PED/NAY	?-g-Cl-Cl

The average error for the data is 1 kJ/mol with a standard deviation of 12 kJ/mol. The largest errors are -28 and +32 kJ/mol. Note the perfluorocyclohexane and the perfluoro 2,7 dimethyloctane are not included in this comparison. The notations g-Cl-Cl, g-Cl-CF₃, etc. refer to gauche interactions. r-6 etc. refer to ring corrections.

TABLE 3 THERMOCHEMICAL GROUPS

Group	Number	Group Value (kJ/mol)
CF, C	16	-690
C-F ₃ C _f	22	-684
C-F ₂ H C	2	-460
C-F ₂ H C _f	7	-444
C-F H ₂ C	2	-222
CH, C	20	-43
C-F ₂ C ₂	1	-460
C-F ₂ C,C	12	-439
C-F ₂ C _{f2}	75	405
C-F H C _f	3	-184
C-F C _f	10	-201
CH, C _f	12	-21
C-F ₂ Cl C	3	-469
CF, Cl C _f	5	-464
C-F ₂ Br C	4	-402
C-F ₂ Br C _f	3	-393
C-F Cl H C	6	-280
C-F Br H C	0	0
C-F Cl Br C	1	-230
C-F Cl ₂ C	6	-264
C-F Br, C	0	0
C-F Cl C _f	1	-183
C-F Br C _f	0	0
C-Cl ₃ C	3	-96
C-Cl, H C	7	-88
C-Cl H ₂ C	9	-67
C-Cl ₂ C _f	1	-88
C-Cl H C _f	3	-54
C-Cl ₂ Br C	0	0
C-Cl Br ₂ C	0	0
C-Cl Br C ₂	0	0
C-Cl Br H C	4	-29
C-Br ₃ C	0	0
C-Br ₂ H C	1	17
C-Br H ₂ C	4	-17
C-Br, C ₂	0	0
C-Br H C ₂	0	0
C-O F Cl C	0	0
C-O F H C	0	0
C-O Cl ₂ C	0	0

TABLE 3: THERMOCHEMICAL GROUPS

Group	Number	Group Value (kJ/mol)
O-C ₂	14	-97
C-H ₂ O C	13	-34
O-H C	6	-159
C-F ₂ O C	16	-448
C-Cl ₃ O	1	-92
CH, O	3	-43
CO-C O	2	-147
O-CO C	2	-180
C-F ₂ C CO	2	-381
C-H ₂ C CO	0	-22
CF, Cl O	1	-519
C-Cl ₂ C O	2	42
<i>gauche</i> -CF ₃ -Cl	4	4
<i>gauche</i> -CF ₃ -Br	0	0
<i>gauche</i> -Cl-Br	4	13
<i>gauche</i> -Cl-Cl	7	13
<i>gauche</i> -Br-Br	0	0
ring-C ₆	3	a
ring-C ₅	0	0
ring-C ₄	0	0
ring-C ₃	0	0
<i>ring-trans</i> -[4.4.0]-C ₁₀	1	-4
<i>ring-cis</i> -[4.4.0]-C ₁₀	1	17
<i>ring-cis</i> -[4.3.0]-C ₉	1	21

Groups with no examples are include for completeness. In order to evaluate all possible halons these groups would need to be defined.