Standard Chemical Thermodynamic Properties of Multichloro Alkanes and Alkenes: A Modified Group Additivity Scheme

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Chlorinated hydrocarbon groups plus non-next-nearest-neighbor interaction terms, which combine with the Benson group additivity method for estimation of thermodynamic properties ($\Delta H_f°$, $S°$ and $C_p(T)$(300−1500 K) on multichloro alkanes and alkenes, are developed. New chlorocarbon alkane and alkene Benson-type group values are derived from molecule systems where no chlorines are on the carbon adjacent to the carbon atom bonded to chlorine(s). A set of interaction terms for $\Delta H_f°$, $S°$, and $C_p(T)$(300−1500 K) is derived to account for non-next-nearest-neighbor chlorine−chlorine interactions. These are derived from the experimental thermodynamic property data on 28 chlorinated hydrocarbons species and current hydrocarbon groups. Thermodynamic properties for representative multichloro alkanes and alkenes determined using this modified group additivity scheme are compared with literature data and show good agreement ($\Delta H_{f°,298} = \pm 0.29$ kcal/mol, $S°_{298} = \pm 0.68$ cal/mol·K, and $C_p(T) = \pm 0.23$ cal/mol·K). The use of a limited number of interaction groups provides improved accuracy in calculation of thermodynamic properties for multichloro alkanes and alkenes when chlorines are on adjacent carbon atoms. We develop three multichloro Benson groups plus five interaction groups for chloroalkanes, and two groups plus five interaction groups for chloroalkenes. This non-next-nearest-neighbor interaction group approach accounts for 13.6 kcal/mol in standard enthalpy for hexachloroethane and 2.7 cal/mol·K in standard entropy for tetrachloroethylene. The multichloro groups combined with the interaction groups allow estimation of thermodynamic properties ($\Delta H_f°$, $S°$, and $C_p(T)$-(300−1500 K)) on larger multichlorocarbon species, where no thermodynamic property data or accurate estimation techniques are available.

Introduction

Chlorocarbons are widely used chemicals or solvents in synthesis and in chemical industry, as starting materials and intermediates in synthesis of polymers, pesticides, and other products. Many chlorocarbons are present in the atmosphere and chlorinated organic species are present in both municipal and hazardous wastes. Thermodynamic properties of chlorocarbons are important to industries utilizing them, in analysis of environmental effects and in evaluation of kinetics or thermodynamic equilibrium for both destruction and synthesis processes. These properties are also needed as input in kinetic modeling and in equilibrium codes.

The presence of chlorocarbon is known to slow the overall oxidation rate of hydrocarbons through studies of flame velocity, temperature, and flame stability.[1] Reports of studies under varied condition sets indicate that both acceleration and inhibition effects can be observed in hydrocarbon reaction systems with a chlorinated hydrocarbon present.[2−4] It would be of significant value to have knowledge of their fundamental thermodynamic properties for equilibria calculations and for an accurate and fundamental understanding of the reaction pathways relating to chlorocarbon formation, destruction, and interactions in synthesis, combustion, and other environmental degradation/transformation processes.

Several techniques are available for estimation of thermodynamic properties data. Ab initio methods may be precise at higher levels, but they are computationally time-intensive. They have difficulty treating large systems and are untested for large chlorocarbon molecules. Semiempirical molecular orbital calculations are faster and require less memory or disk capacity than ab initio but are not of sufficient accuracy for $\Delta H_f°$'s. Dewar et al.[9] compared AM1 calculation results with the experimental data for 157 halogen-containing molecules. The AM1 errors in heats of formation for more than 60 compounds were larger than ±5 kcal/mol, and the average error for organic halides was 4.39 kcal/mol. Li Zhu et al.[20] found similar or larger errors for MOPAC6 PM3 calculations[21] on chlorocarbon and chlorohydrocarbon compounds.

Benson's group method[5−8] has been widely used to estimate enthalpies of formation and Gibbs free energies of reactions for many organic species. Group additivity is easy to use; it is based on experimental data and known to be accurate for hydrocarbons.[10,11] Benson's group values do not, however, fully account for the steric or electrostatic interactions between adjacent bulky groups or atoms such as methyls, chlorines, or other halogens on aromatics or alkyl chains when used for the estimation of thermodynamic properties ($\Delta H_f°$, $S°$, and $C_p(T)$-(300−1500 K)) of these molecules. These interactions are termed non-next-nearest-neighbor interactions because they arise from the substituents on two adjacent central atoms: a central atom is defined by Benson[5] as an atom bonded to two or more substituents.

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TABLE 1: Comparison of Enthalpy of Formation and Entropy at 298 K Incorporating New Chlorocarbon Group Values[a,b]

					group calc.	
group	compounds	Stull[15]	TRC[16]	Pedley[17]	Benson/Cohen	non-next-nearest neighbor (this work)
	Enthalpies of Formation at 298 K					
C/C/Cl$_2$/H	1,1-dichloroethane	−31.05	−31.10	−30.52	−27.90	−31.04
	1,1-dichloropropane		−36.03		−32.90	−36.04
	1,1-dichlorobutane		−40.96		−37.90	−41.04
	1,1-dichloropentane		−45.89		−42.90	−46.04
	1,1-dichlorohexane		−50.82		−47.90	−51.04
	1,3 dichloropropane	−38.60		−38.05	−38.40	*d*
C/C$_2$/Cl$_2$	2,2-dichloropropane	−42.00		−41.40	−41.40	−42.00
C/C/Cl$_3$	1,1,1-trichloroethane		−34.01		−28.00	−33.84
	1,1,1-trichloropropane		−38.94		−33.00	−38.84
	1,1,1-trichlorobutane		−43.88		−38.00	−43.84
	1,1,1-trichloropentane		−48.80		−43.00	−48.84
	1,1,1-trichlorohexane		−53.73		−48.00	−53.84
CD/Cl$_2$	1,1-dichloroethylene	0.30	0.57	0.62	4.56	0.50
CD/CD/Cl	2-chloro-1,3-butadiene		6.64		NA	5.56
	2,3-dichloro-1,3-butadiene		−12.98		NA	−12.44
	1,1,2-trichloro-1,3-butadiene		−2.21		NA	−1.39
INT/Cl$_2$	1,2-dichloroethane	−31.00	−30.30	−30.33	−33.40	−31.05
	1,2-dichloropropane	−39.60		−38.91	−41.30	−38.72
INT/Cl$_3$	1,1,2-trichloroethane	−33.10	−34.56	−34.80	−34.60	−33.99
	1,2,3-trichloropropane	−44.40		−43.71	−48.00	−44.22
INT/Cl$_4$	1,1,1,2-tetrachloroethane		−35.71		−34.70	−35.54
	1,1,2,2-tetrachloroethane	−36.50	−35.61	−35.66	−35.80	−36.98
INT/Cl$_5$	pentachloroethane	−34.00			−35.90	−34.00
INT/Cl$_6$	hexachloroethane	−33.80		−34.32	−36.00	−34.06
INT/CD/Cl$_2$	1,2-(*Z*)-dichloroethylene	0.45	−0.67	1.10	1.2	0.30
	1,2-(*E*)-dichloroethylene	1.00	−0.10	1.20	2.2	0.70
INT/CD/Cl$_3$	trichloroethylene	−1.40	−1.94	−2.30	−1.1	−1.88
INT/CD/Cl$_4$	tetrachloroethylene	−3.40	−2.90		−3.4	−3.15
	Entropies of Formation at 298 K					
C/C/Cl$_2$/H	1,1-dichloroethane ⟨3⟩[c]	72.89	72.91		71.82	73.03
	1,1-dichloropropane ⟨3⟩		82.39		81.22	82.43
	1,1-dichlorobutane ⟨3⟩		91.87		90.62	91.83
	1,1-dichloropentane ⟨3⟩		101.36		100.02	101.23
	1,1-dichlorohexane ⟨2⟩		110.85		109.42	110.63
	1,3-dichloropropane ⟨18⟩	83.91			83.62	*d*
C/C$_2$/Cl$_2$	2,2-dichloropropane ⟨3⟩	77.92			77.26	77.92
C/C/Cl$_3$	1,1,1-trichloroethane ⟨9⟩		76.49		76.33	76.62
	1,1,1-trichloropropane ⟨9⟩		85.97		85.73	86.02
	1,1,1-trichlorobutane ⟨9⟩		95.46		95.13	95.42
	1,1,1-trichloropentane ⟨9⟩		104.95		104.53	104.82
	1,1,1-trichlorohexane ⟨9⟩		114.43		113.93	114.22
CD/Cl$_2$	1,1-dichloroethylene ⟨2⟩	68.85	67.90		69.71	67.00
CD/CD/Cl	2-chloro-1,3-butadiene ⟨1⟩		74.91		NA	76.07
	2,3-dichloro-1,3-butadiene ⟨2⟩		79.87		NA	81.49
	1,1,2-trichloro-1,3-butadiene ⟨1⟩		92.70		NA	90.73
INT/Cl$_2$	1,2-dichloroethane ⟨1⟩	73.66	73.10		76.34	75.05
	1,2-dichloropropane ⟨3⟩	84.00			83.52	82.33
INT/Cl$_3$	1,1,2-trichloroethane ⟨1⟩	80.57	79.69		81.50	81.22
	1,2,3-trichloropropane ⟨2⟩	91.52			91.82	90.43
INT/Cl$_4$	1,1,1,2-tetrachloroethane ⟨3⟩		85.05		86.02	84.53
	1,1,2,2-tetrachloroethane ⟨2⟩	86.69	84.84		86.02	86.29
INT/Cl$_5$	pentachloroethane ⟨3⟩	90.95			91.92	90.95
INT/Cl$_6$	hexachloroethane ⟨18⟩	94.77			95.06	94.77
INT/CD/Cl$_2$	1,2-(*Z*)-dichloroethylene ⟨2⟩	69.20	69.22		69.42	69.21
	1,2-(*E*)-dichloroethylene ⟨2⟩	69.29	69.28		69.42	69.29
INT/CD/Cl$_3$	trichloroethylene ⟨1⟩	77.63	77.70		77.50	77.67
INT/CD/Cl$_4$	tetrachloro ethylene ⟨4⟩	81.46	81.47		81.45	81.47

[a] Benson/Cohen hydrocarbon groups and corresponding chloroalkane and alkene groups. [b] Units: $\Delta H_f°$, kcal/mol; $S°$, and C_p, cal/(mol·K). [c] ⟨#⟩ external symmetry number. [d] No interaction term.

Procedure

Selection (definition) of the initial groups is critical to development of a group additivity scheme for accurate property estimation. It is also important to note that previous group additivity approaches for chlorocarbons did not incorporate effects of non-next-nearest neighbors. Consider the two molecules 1,1-dichloroethane and 1,2-dichloroethane and the groups that are used to estimate the thermodynamic properties.

	1,1-dichloroethane CH_3-CHCl_2	1,2-dichloroethane CH_2Cl-CH_2Cl
groups	C/C/Cl$_2$/H	C/C/Cl/H$_2$
	C/C/H$_3$	C/C/Cl/H$_2$

TABLE 2: Group Values[e]

group	$\Delta H_f°{}_{,298}$	$S°_{298}$	C_p (T/K)						
			300	400	500	600	800	1000	1500
a. Benson/Cohen Hydrocarbon Groups (Recommended[10,11] Values)[f]									
$C/C/H_3$	−10.00	30.30	6.19	7.84	9.40	10.79	13.02	14.77	17.58
$C/C_2/H_2$	−5.00	9.40	5.50	6.95	8.25	9.35	11.07	12.34	14.20
$C/C_3/H$	−2.40	−12.30	4.54	6.00	7.17	8.05	9.31	10.05	11.18
C/C_4	−0.10	−35.00	4.37	6.13	7.36	8.12	8.77	8.76	8.12
CD/H_2[a]	6.26	27.61	5.10	6.36	7.51	8.50	10.07	11.27	13.19
CD/CD/H[a]	6.78	6.38	4.46	5.79	6.75	7.42	8.35	9.11	10.13
GAUCHE (Cohen)	0.80	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
b. Chlorocarbon Groups for Multichloro Alkane and Alkene Groups[b]									
$C/C/Cl/H_2$[c]	−16.80	38.17	8.74	10.54	12.08	13.31	15.15	16.47	18.46
$C/C_2/Cl/H$[c]	−14.47	17.33	8.47	10.20	11.68	12.76	14.29	15.38	16.21
$C/C_3/Cl$[c]	−14.03	−6.45	8.09	10.15	11.69	12.65	13.47	13.53	13.32
$C/C/Cl_2/H$	−21.04	44.91	11.99	13.98	15.53	16.62	18.09	18.80	19.43
$C/C_2/Cl_2$	−22.00	23.06	13.12	14.88	15.95	16.48	16.96	17.02	16.82
$C/C/Cl_3$	−23.84	50.69	15.83	17.86	19.25	20.10	21.06	21.21	21.42
CD/CD/Cl	−13.76	14.47	7.23	8.86	9.66	10.26	10.96	11.28	11.52
CD/Cl_2	−5.76	40.77	10.97	12.42	13.33	13.92	14.63	15.01	15.44
CD/Cl/H[a]	−1.20	35.40	7.90	9.20	10.30	11.20	12.30	13.10	14.25
CD/C/Cl[d]	−2.10	15.0	8.00	8.40	8.50	9.00	9.20	9.40	9.57
c. Interaction Groups for Multichloro Alkane and Alkene Groups[b]									
INT/Cl_2	2.54	−1.29	0.75	0.46	0.23	0.08	−0.05	−0.05	0.02
INT/Cl_3	3.85	−1.86	0.58	0.33	0.04	−0.12	−0.24	−0.24	0.2
INT/Cl_4	5.10	−2.15	0.05	−0.11	−0.26	−0.24	−0.10	0.43	0.73
INT/Cl_5	10.88	−2.47	0.45	0.02	−0.31	−0.44	−0.53	0.02	0.18
INT/Cl_6	13.62	−0.87	1.06	0.44	−0.15	−0.44	−0.73	−0.17	0.47
CIS/Cl/Cl	−0.4	−0.08	−0.37	−0.17	−0.09	−0.05	−0.01	−0.01	0.0
$Z/Cl/CD_3$	18.01	0.65	0.24	−0.76	−0.60	−0.47	−0.51	−0.40	−0.61
$INT/CD/Cl_2$	3.10	−0.13	0.16	0.15	0.03	−0.15	−0.02	0.02	0.13
$INT/CD/Cl_3$	5.08	1.50	0.39	0.18	0.04	−0.06	0.01	0.04	0.1
$INT/CD/Cl_4$	8.37	2.68	0.79	0.26	0.06	0.02	0.02	0.05	0.09
GAUCHE-Cl	1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

[a] Reference 5. [b] Use with the Benson/Cohen recommended[10,11] values. [c] Reference 14. [d] $\Delta H_f°{}_{298}$ and $S°_{298}$ are from ref 5. Heat capacities are from ref 8. [e] Units: $\Delta H_f°$, kcal/mol; $S°$ and C_p, cal/(mol·K). [f] Heat capacities are those of Benson for all cases.

In the 1,1-dichloroethane isomer, the $C/C/Cl_2/H$ group incorporates polar and steric interactions between the two chlorines as well as adjacent hydrogens and carbons on the central carbon atom. The 1,2-dichloroethane isomer $C/C/Cl/H_2$ groups do not include or incorporate any interactions (polar, steric, ..., etc.) between the two chlorines.

We derive a new set of groups for chlorocarbon alkanes and alkenes from the experimental thermodynamic property data on respective chlorinated hydrocarbons. The groups are derived from literature data on molecules where there are only carbon or hydrogen atoms on carbons that are adjacent to the carbon atom bonded to chlorine(s). The $C/C/Cl/H_2$, $C/C/Cl_2/H$, or $C/C/Cl_3$ groups are derived from chloroethane (CH_3CH_2Cl), 1,1-dichloroethane (CH_3CHCl_2), and 1,1,1-trichloroethane (CH_3-CCl_3), respectively. There are no chlorines, other halogens, or bulky groups/fragments on the carbon atom(s) adjacent to the carbon atom containing the chlorines in the defining group. The $C/C/Cl_3$ group, for example, is defined from the parent 1,1,1-trichloroethane, and the $C/C/H_3$ group from hydrocarbon properties. Similarly CD/Cl/H and CD/Cl_2 groups are derived from chloroethylene ($CH_2{=}CHCl$) and 1,1-dichloroethylene ($CH_2{=}CCl_2$), respectively. Thermodynamic properties of chlorocarbons with no Cl on the carbon atoms adjacent to a carbon with Cl are now accurately predicted, but an adjustment needs to be made for chlorocarbon species where there is a Cl (or other halogen) on an adjacent carbon, such as 1,2-dichloroethane, or 1,1,2-trichloroethylene. This adjustment comes in the form of an interaction group to count the total number of Cl atoms (that interact) on each of the two adjacent carbon atoms. There is no interaction group when the Cl atoms are only on one of the carbons. We choose an additive scheme for number of chlorines; thus, $CCl_3{-}CCl_3$ has six interactions, not nine.

Our assumption is based on the known accuracy and validity of group additivity for hydrocarbon and oxyhydrocarbons[7,10−12] with gauche interactions. Conventional group additivity does not, however, work for chlorocarbons. This is readily observed in comparison of enthalpies estimated by published Benson group values with experimental data illustrated in the enthalpy sections of Table 1.

One alternate method to correct for non-next-nearest-neighbor effects on adjacent carbons is the use of gauche interactions.[5] This method is not, however, appropriate for chlorocarbon species. 1,2-Dichloroethane, for example, has no Cl−Cl gauche interaction but needs a correction (interaction term) of 2.54 kcal/mol to obtain the correct $\Delta H°_{f,298}$ by group additivity using the $C/C/Cl/H_2$ group determined in this study (see below).

In our previous work, interaction terms for multiple Br, Cl, F, CH_3, and OH substituents on aromatic compounds[13] and a set of groups for monochloroalkanes[14] have been developed. In this paper, we derive new chlorocarbon groups that can be used with the Benson group additivity scheme for calculation of the thermodynamic properties of multichloro alkanes and alkenes. Our method requires the inclusion of non-next-neighbor interaction terms (groups) when chlorine atoms are on carbons adjacent to a carbon bonded to one or more chlorine(s).

A multichloro group is derived by choosing representative molecules and their literature[15−17] thermodynamic properties $\Delta H_f°$, $S°$, and $Cp(T)$(300−1500 K). The molecules contain the same multichloro groups with no chlorines or other halogens on adjacent carbons. Average deviations in thermodynamic

TABLE 3: Heat Capacity Comparison of TRC Recommended Heat Capacities to Group Data[b]

group	compound	C_p (T/K)						
		300	400	500	600	800	1000	1500
a. Multichloro Benson Groups								
TRC Data								
C/C/Cl$_2$/H	1,1-dichloroethane	18.32	21.87	24.81	27.23	30.79	33.40	37.35
	1,1-dichloropropane	23.75	28.78	33.11	36.64	42.02	45.82	51.72
	1,1-dichlorobutane	29.18	35.72	41.43	46.11	53.25	58.25	66.09
	1,1-dichloropentane	34.62	42.66	49.75	55.55	64.47	70.67	80.46
	1,1-dichlorohexane	40.05	49.60	58.07	65.01	75.70	83.09	94.83
	1,3-dichloropropane[a]	22.93	28.69	32.82	36.22	41.56	45.50	
C/C$_2$/Cl$_2$	2,2-dichloropropane	25.40	30.56	34.75	38.06	43.00	46.56	
C/C/Cl$_3$	1,1,1-trichloroethane	22.14	25.71	28.51	30.68	33.75	35.81	38.80
	1,1,1-trichloropropane	27.58	32.66	36.84	40.13	44.98	48.23	53.17
	1,1,1-trichlorobutane	33.01	39.60	45.16	49.59	56.20	60.66	67.54
	1,1,1-trichloropentane	38.45	46.53	53.48	59.05	67.43	73.09	81.91
	1,1,1-trichlorohexane	43.88	53.48	61.80	68.51	78.65	85.51	96.28
CD/Cl$_2$	1,1-dichloroethylene	16.05	18.76	20.82	22.40	24.68	26.26	28.63
CD/CD/Cl	2-chloro-1,3-butadiene	22.21	27.35	31.44	34.70	39.52	42.98	
	2,3-dichloro-1,3-butadiene	25.25	30.50	34.49	37.57	41.96	45.03	
	1,1,2-trichloro-1,3-butadiene	29.40	33.84	37.31	40.04	43.98	46.67	
Group Additivity Values, This Work								
C/C/Cl$_2$/H	1,1-dichloroethane	18.18	21.82	24.93	27.41	31.11	33.57	37.01
	1,1-dichloropropane	23.68	28.77	33.18	36.76	42.18	45.91	51.21
	1,1-dichlorobutane	29.18	35.72	41.43	46.11	53.25	58.25	65.41
	1,1-dichloropentane	34.68	42.67	49.68	55.46	64.32	70.59	79.61
	1,1-dichlorohexane	40.18	49.62	57.93	64.81	75.39	82.93	93.81
	1,3-dichloropropane[a]	22.98	28.03	32.41	35.97	41.37	45.28	51.12
C/C$_2$/Cl$_2$	2,2-dichloropropane	25.50	30.56	34.75	38.06	43.00	46.56	51.98
C/C/Cl$_3$	1,1,1-trichloroethane	22.02	25.70	28.65	30.89	34.08	35.98	39.00
	1,1,1-trichloropropane	27.52	32.65	36.90	40.24	45.15	48.32	53.00
	1,1,1-trichlorobutane	33.02	39.60	45.15	49.59	56.22	60.66	67.40
	1,1,1-trichloropentane	38.52	46.55	53.40	58.94	67.29	73.00	81.60
	1,1,1-trichlorohexane	44.02	53.50	61.65	68.29	78.36	85.34	95.80
CD/Cl$_2$	1,1-dichloroethylene	16.07	18.78	20.84	22.42	24.70	26.28	28.63
CD/CD/Cl	2-chloro-1,3-butadiene	21.99	27.15	31.32	34.67	39.57	42.20	48.03
	2,3-dichloro-1,3-butadiene	25.45	30.51	34.52	37.67	42.13	45.04	49.43
	1,1,2-trichloro-1,3-butadiene	28.16	33.23	37.15	40.15	44.19	46.67	50.38
b. Interaction Groups								
TRC Data								
INT/Cl$_2$	1,2-dichloroethane	18.77	21.98	24.83	27.18	30.78	33.39	37.64
	1,2-dichloropropane	23.60	28.60	32.95	36.47	41.97	46.08	
INT/Cl$_3$	1,1,2-trichloroethane	20.87	24.75	27.83	30.21	33.57	35.78	39.29
	1,2,3-trichloropropane	26.96	31.71	35.69	38.87	43.79	47.34	
INT/Cl$_4$	1,1,1,2-tetrachloroethane	24.69	28.36	31.16	33.28	36.24	38.17	40.70
	1,1,2,2-tetrachloroethane	23.95	27.79	30.71	32.90	35.92	37.89	40.66
INT/Cl$_5$	pentachloroethane	28.27	31.86	34.47	36.28	38.62	40.03	42.00
INT/Cl$_6$	hexachloroethane	32.72	36.16	38.35	39.76	41.39	42.25	43.31
INT/CD/Cl$_2$	1,2-(Z) dichloroethylene	15.59	18.37	20.53	22.20	24.57	26.20	28.63
	1,2-(*E*)-dichloroethylene	15.95	18.54	20.62	22.25	24.59	26.21	28.63
INT/CD/Cl$_3$	trichloroethylene	19.26	21.80	23.67	25.06	26.94	28.15	29.79
INT/CD/Cl$_4$	tetrachloroethylene	22.73	25.10	26.72	27.86	29.28	30.07	30.97
Group Additivity Values, This Work								
INT/Cl$_2$	1,2-dichloroethane	18.23	21.54	24.39	26.70	30.25	32.89	36.94
	1,2-dichloropropane	24.15	29.04	33.39	36.94	42.41	46.57	52.27
INT/Cl$_3$	1,1,2-trichloroethane	21.31	24.85	27.65	29.81	33.00	35.03	38.09
	1,2,3-trichloropropane	26.53	31.61	35.88	39.26	44.35	48.08	53.33
INT/Cl$_4$	1,1,1,2-tetrachloroethane	24.62	28.29	31.07	33.17	36.11	38.11	40.61
	1,1,2,2-tetrachloroethane	24.03	27.85	30.80	33.00	36.08	38.03	39.59
INT/Cl$_5$	pentachloroethane	28.27	31.86	34.47	36.28	38.62	40.03	41.03
INT/Cl$_6$	hexachloroethane	32.72	36.16	38.35	39.76	41.39	42.25	43.31
INT/CD/Cl$_2$	1,2-(*Z*)-dichloroethylene	15.66	18.34	20.49	22.20	24.65	26.26	28.65
	1,2-(*E*)-dichloroethylene	15.96	18.55	20.63	22.25	24.58	26.22	28.63
INT/CD/Cl$_3$	trichloroethylene	19.26	21.80	23.67	25.06	26.94	28.15	29.79
INT/CD/Cl$_4$	tetrachloro ethylene	22.73	25.10	26.72	27.86	29.28	30.07	30.97

[a] No interaction term. [b] Units: C_p, cal/(mol·K); temperature, K.

values determined by group additivity and the literature are obtained.

$$X_{\mathrm{ClC\ group}} = X_{\mathrm{expt}} - \Sigma X_{\mathrm{HC\ group}}$$

where X represents the specific enthalpy, entropy, or heat capacity property. $X_{\mathrm{ClC\ group}}$ is the chlorocarbon group. X_{expt} is the corresponding experimental or literature value. $\Sigma X_{\mathrm{HC\ group}}$ is the sum of the hydrocarbon groups in the molecule.

Deviations between group additivity values and literature values are minimized when more than one molecule with known

TABLE 4: Example Calculations of Thermodynamic Properties for More Complex Chlorocarbons

								C_p (T/K)					
Gr #	GROUP ID	quantity	CPINF	NROTORS	SYMMETRY	$\Delta H_f{}^\circ{}_{,298}$	$S^\circ{}_{298}$	300	400	500	600	800	1000
Hexachloro-1,3-butadiene, C_4Cl_6													
1	CD/CD/Cl	2	54.64	1	4	−8.33	110.09	38.17	42.62	45.69	47.85	50.64	52.21
2	CD/Cl2	2											
3	INT/Cl2	1											
4	INT/CD/Cl3	2											
5	Z/Cl/CD3	1											
1,1,2,4,4-Pentachloro-1,3-butadiene, C_4HCl_5													
1	CD/Cl2	2	54.64	1	1	7.69	104.41	34.42	39.06	42.54	44.84	48.05	50.07
2	CD/CD/H	1											
3	CD/CD/Cl	1											
4	INT/CD/Cl2	1											
5	INT/CD/Cl3	1											
6	Z/Cl/CD3	1											
trans-1,1,2,3,4-Pentachloro-1,3-butadiene, C_4HCl_5													
1	CD/Cl/H	1	54.64	1	1	−5.75	105.84	34.87	39.37	42.65	45.04	48.28	50.28
2	CD/Cl2	1											
3	CD/CD/Cl	2											
4	INT/Cl2	1											
5	INT/CD/Cl2	1											
6	INT/CD/Cl3	1											
7	Z/Cl/CD3	1											
1,1,2,4,4-Pentachloro-2,3-butadiene, C_4HCl_5													
1	CD/Cl_2	1	54.64	1	1	10.45	104.17	35.82	39.76	42.24	44.46	46.95	48.44
2	CA	1											
3	CD/C/Cl	1											
4	C/CD/Cl2/H	1											
5	INT/Cl3	1											
6	GAUCHE-Cl	1											
1,1,2,3,3,4,4-Heptachlorobutylene, C_4Cl_7H													
1	CD/Cl2	1	65.57	2	1	−34.03	120.33	45.48	50.45	53.48	55.82	58.64	60.54
2	CD/C/Cl	1											
3	C/C/CD/Cl2	1											
4	C/C/Cl2/H	1											
5	INT/Cl3	1											
6	INT/Cl4	1											
7	INT/CD/Cl3	1											
8	GAUCHE-Cl	1											
1,1,2,3,4,4,4-Heptachlorobutylene, C_4Cl_7H													
1	CD/Cl2	1	65.57	2	3	−30.61	120.95	44.84	49.78	53.12	55.78	59.13	61.50
2	CD/C/Cl	1											
3	C/C/CD/Cl/H	1											
4	C/C/Cl3	1											
5	INT/Cl2	1											
6	INT/Cl4	1											
7	INT/CD/Cl3	1											
8	GAUCHE-Cl	1											

[a] Units: $\Delta H_f{}^\circ$, kcal/mol; S° and C_p, cal/(mol•K).

thermodynamic properties is available for the group derivation. The multichlorocarbon groups result from minimization of the average deviations. The multichlorocarbon groups developed for use with the respective Benson/Cohen hydrocarbon groups (HC) are listed in Table 2b. We choose the recent hydrocarbon (HC) group values published by Benson and Cohen[10,11] for use in the derivation of our new HClC group data. The hydrocarbon (HC) group values of Benson and Cohen are listed in Table 2a. $R \ln(\sigma)$, where σ is symmetry of the parent chloro hydrocarbon, is added to the S value of the molecule in order to obtain the intrinsic entropy group values.

Thermodynamic properties of multichloro alkanes and alkenes with chlorine on adjacent carbons such as 1,2-dichloroethane are then further corrected by use of interaction terms that account for non-next-nearest-neighbor interactions between the Cl substituents. Molecules having the same number (total) of these type of interactions are grouped together. $X_{INT} = X_{expt} - X_{Ga}$, where X_{INT} is the interaction group.

The interaction group is based on the average thermo-value deviations for molecules in the grouping (same number of interactions). The nomenclature used is in terms of a general interaction: abbreviation (INT). For example, INT/Cl_2 indicates two adjacent Cl interactions, as in 1, 2 dichloroethane. Interaction groups developed for use with the respective Benson/Cohen hydrocarbon groups (HC) are listed in Table 2c.

Discussion

Table 1 shows comparisons of $\Delta H_f{}^\circ{}_{,298}$ and $S^\circ{}_{298}$ using the Benson and the newly derived (this work) group additivity with literature data of Stull,[15] TRC,[16] and Pedley[17] for the relevant chlorocarbons. Table 3 compares the heat capacity from our group additivity with the data from TRC[16] for the temperatures 300, 400, 500, 600, 800, and 1000 K. In each table, the compounds selected for calculation of the group value are followed by the compounds that require interaction terms. While the data

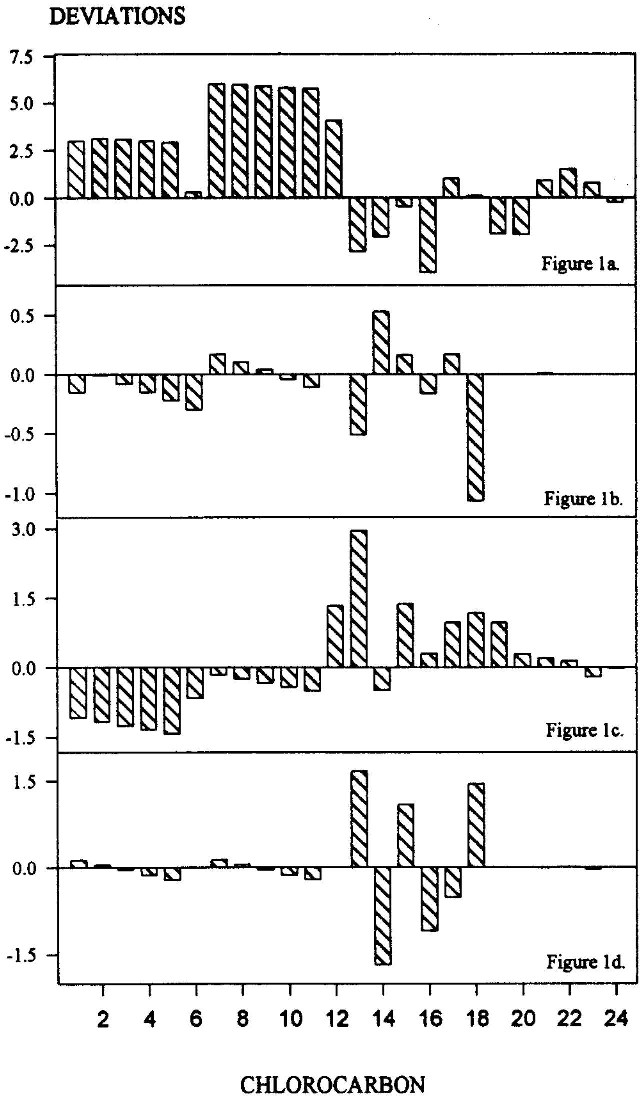


Figure 1. (a) Enthalpy deviations between values calculated by using published Benson groups vs literature values for $\Delta H_f°_{,298}$. (b) Enthalpy deviations between values calculated by using newly derived (this work) groups with interaction terms verses literature values for $\Delta H_f°_{,298}$. (c) Entropy deviations between values calculated by using published Benson groups vs literature values for entropy at 298 K. (d) Entropy deviations between values calculated by using newly derived (this work) groups and literature values for entropy at 298 K. Units: $\Delta H_f°_{,298}$, kcal/mol; entropy, cal/(mol•K). Key: (1) 1,1-dichloroethane, (2) 1,1-dichloropropane, (3) 1,1-dichlorobutane, (4) 1,1-dichloropentane, (5) 1,1-dichlorohexane, (6) 2,2-dichloropropane, (7) 1,1,1-trichloroethane, (8) 1,1,1-trichloropropane, (9) 1,1,1-trichlorobutane, (10) 1,1,1-trichloropentane, (11) 1,1,1-trichlorohexane, (12) 1,1-dichloroethylene, (13) 1,2-dichloroethane, (14) 1,2-dichloropropane, (15) 1,1,2-trichloroethane, (16) 1,2,3-trichloropropane, (17) 1,1,1,2-tetrachloroethane, (18) 1,1,2,2-tetrachloroethane, (19) pentachloroethane, (20) hexachloroethane, (21) 1,2-(*E*)-dichloroethylene, (22) 1,2-(*Z*)-dichloroethylene, (23) trichloroethylene, (24) tetrachloroethylene.

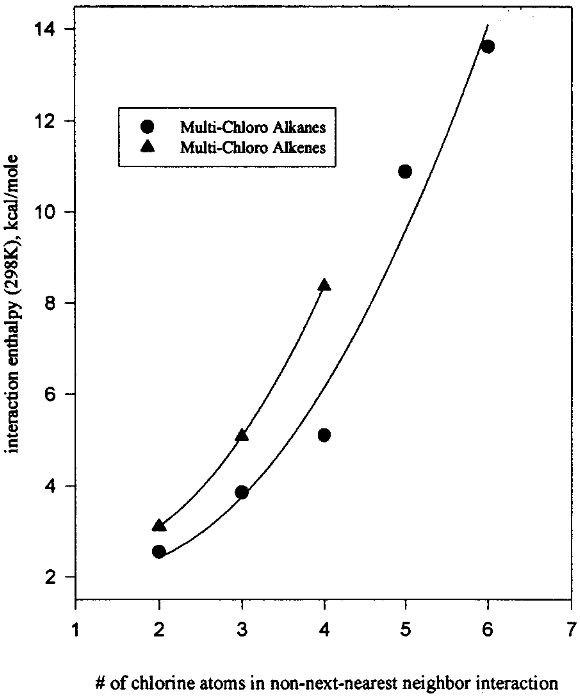


Figure 2. Interaction enthalpies as a function of number of interactions for multichloro alkanes and alkenes.

TABLE 5: Enthalpy Interaction Correction on a per Chlorine Base

group	enthalpy interaction per Cl, kcal/mol
INT/Cl_2	1.27
INT/Cl_3	1.28
INT/Cl_4	1.28
INT/Cl_5	2.18 (1.81[a])
INT/Cl_6	2.27 (1.51[b])
INT/CD/Cl_2	1.55
INT/CD/Cl_3	1.69
INT/CD/Cl_4	2.09

[a] Multiplicative number of interactions = 6. [b] Multiplicative number of interactions = 9.

in each table are presented to two significant decimal places, they are not accurate to this degree. They are meant only for inclusion in developing computer codes for use in calculating molecule and radical thermodynamic properties and other applications where rounding off can be effected at the end of the summation.

Enthalpies, entropies, and heat capacities as a function of temperature for any species can be easily determined manually or by THERM.[18] THERM also extrapolates data to 5000 K and calculates ΔG_{rxn} and equilibrium constants. The groups, interaction terms, symmetry correction, and number of number internal rotors for the 28 reference species are listed in Tables 6 and 7 (internal rotors are used to adjust C_p $T = \infty$).[19] Table 4 estimates and gives example calculations for six larger and more complex multichloro species.

Parts a and c of Figure 1 illustrate the deviations between values by using published Benson groups and literature values for $\Delta H_f°_{,298}$ (kcal/mol) and $S°_{298}$ (cal/mol•K), respectively, for the 24 reference multichloro alkanes and alkenes. Deviations range from −3.95, 1,2,3-trichloroethane, to 6.01 kcal/mol, 1,1,1-trichloroethane, in $\Delta H_f°_{,298}$ and from −1.43, 1,1-dichlorohexane, to 2.96 cal/mol•K, 1,2-dichloroethane for entropy. Parts b and d of Figure 1 illustrate the deviations for $\Delta H_f°_{,298}$ and $S°_{298}$, respectively, between values from our multichloro group values with interaction terms and literature measurements. Deviations are less than 1.06 kcal/mol, 1,1,2,2-tetrachloroethane, for $\Delta H_f°_{,298}$ and 1.67 cal/mol•K, 1,2-dichloropropane, for $S°_{298}$.

The interaction of chlorines across a carbon−carbon bond is accounted for by an interaction (correction) term. Figure 2 illustrates that higher chlorinated species have stronger or increased interactions and that the correction increase is near quadratic with the number of interactions. For example, heat of formation for C_2Cl_6 using only nearest-neighbor groups (groups derived in this work with no interaction group) is ca. 13 kcal/mol lower than the experimental data; the C_2Cl_6 molecule has six Cl interactions. Table 5 lists the enthalpy

TABLE 6: Groups and Interaction Terms Used in Calculations of Thermodynamic Properties for Chlorocarbons

name	formula	symm.[a]	rotor[b]	group ID	quant.	group ID	quant.	group ID	quant.	group ID	quant.	group ID	quant.
1,1-dichlrooethane	C2H4CL2	3	1	C/C/H3	1	C/C/CL2/H	1						
1,1-dichloropropane	C3H6CL2	3	2	C/C/H3	1	C/C2/H2	1	C/C/CL2/H	1				
1,1-dichlorobutane	C4H8CL2	3	3	C/C/H3	1	C/C2/H2	1	C/C2/H2	1	C/C/CL2/H	1		
1,1-dichloropentane	C5H10CL2	3	4	C/C/H3	1	C/C2/H2	1	C/C2/H2	1	C/C2/H2	1	C/C/CL2/H	1
1,1-dichlorohexane	C6H12CL2	3	5	C/C/H3	1	C/C2/H2	4	C/C/CL2/H	1				
1,2-dichloroethane	C2H4CL2	1	1	C/C/CL/H2	1	C/C/CL/H2	1	INT/CL2	1				
1,2-dichloropropane	C3H6CL2	3	2	C/C/CL/H2	1	C/C2/CL/H	1	C/C/H3	1	INT/CL2	1		
1,1-dichloroethylene	C2H2CL2	2	0	CD/CL2	1	CD/H2	1						
1,2-(*E*)-dichloroethylene	C2H2CL2	2	0	CD/CL/H	1	CD/CL/H	1	INT/CD/CL2	1				
1,2-(*Z*)-dichloroethylene	C2H2CL2	2	0	CD/CL/H	2	INT/CD/CL2	1	CIS/CL/CL	1				
2,2-dichloropropane	C3H6CL2	18	2	C/C/H3	2	C/C2/CL2	1						
1,1,2-trichloroethane	C2H3CL3	1	1	C/C/CL/H2	1	C/C/CL2/H	1	INT/CL3	1				
1,2,3-trichloropropane	C3H5CL3	2	2	C/C/CL/H2	2	C/C2/CL/H	1	INT/CL3	1				
1,1,2,2-tetrachloroethane	C2H2CL4	2	1	C/C/CL2/H	2	INT/CL4	1						
1,3-dichloropropane	C3H6CL2	2	2	C/C/CL/H2	2	C/C2/H2	1						
1,1,1,2-tetrachloroethane	C2H2CL4	3	1	C/C/CL3	1	C/C/CL/H2	1	INT/CL4	1				
1,1,1-trichloroethane	C2H3CL3	9	1	C/C/H3	1	C/C/CL3	1						
1,1,1-trichloropropane	C3H5CL3	9	2	C/C/H3	1	C/C2/H2	1	C/C/CL3	1				
1,1,1-trichlorobutane	C4H7CL3	9	3	C/C/H3	1	C/C2/H2	2	C/C/CL3	1				
1,1,1-trichloropentane	C5H9CL3	9	4	C/C/H3	1	C/C2/H2	3	C/C/CL3	1				
1,1,1-trichlorohexane	C6H11CL3	9	5	C/C/H3	1	C/C2/H2	4	C/C/CL3	1				
pentachloroethane	C2HCL5	3	1	C/C/CL2/H	1	C/C/CL3	1	INT/CL5	1				
hexachloroethane	C2CL6	18	1	C/C/CL3	2	INT/CL6	1						
trichloroethylene	C2HCL3	1	0	CD/CL/H	1	CD/CL2	1	INT/CD/CL3	1				
tetrachloroethylene	C2CL4	4	0	CD/CL2	2	INT/CD/CL4	1						
2-chloro-1,3-butadiene	C4H5CL	1	1	CD/H2	2	CD/CD/CL	1	CD/CD/H	1				
2,3-dichloro-1,3-butadiene	C4H4CL2	2	1	CD/H2	2	CD/CD/CL	2	INT/CL2	1				
1,1,2-trichloro-1,3-butadiene	C4H3CL3	1	1	CD/H2	1	CD/CL2	1	CD/CD/CL	1	CD/CD/H	1	INT/CD/CL3	1

[a] External symmetry number. [b] Number of internal rotors.

TABLE 7: Listing of Thermodynamic Properties Data for Species in Table 6[a]

name	H_f	S	C_p						
			300	400	500	600	800	1000	1500
1,1-dichlrooethane	−31.04	73.03	18.18	21.82	24.93	27.41	31.11	33.57	37.01
1,1-dichloropropane	−36.04	82.43	23.68	28.77	33.18	36.76	42.18	45.91	51.21
1,1-dichlorobutane	−41.04	91.83	29.18	35.72	41.43	46.11	53.25	58.25	65.41
1,1-dichloropentane	−46.04	101.23	34.68	42.67	49.68	55.46	64.32	70.59	79.61
1,1-dichlorohexane	−51.04	110.63	40.18	49.62	57.92	64.81	75.39	82.93	93.81
1,2-dichloroethane	−31.05	75.05	18.23	21.54	24.39	26.70	29.78	32.89	36.94
1,2-dichloropropane	−38.72	82.33	24.15	29.04	33.39	36.94	41.94	46.57	52.27
1,1-dichloroethylene	0.50	67.00	16.07	18.78	20.84	22.42	24.70	26.28	28.67
1,2-(*E*)-dichloroethylene	0.70	69.29	15.96	18.55	20.63	22.25	24.58	26.22	28.63
1,2-(*Z*)-dichloroethylene	0.30	69.21	15.66	18.34	20.49	22.20	24.65	26.26	28.65
2,2-dichloropropane	−42.00	77.92	25.50	30.56	34.75	38.06	43.00	46.56	51.98
1,1,2-trichloroethane	−33.99	81.22	21.31	24.85	27.65	29.81	33.00	35.03	38.09
1,2,3-trichloropropane	−44.22	90.43	26.53	31.61	35.88	39.26	44.35	48.08	53.33
1,1,2,2-tetrachloroethane	−36.98	86.29	24.03	27.85	30.80	33.00	36.08	38.03	39.59
1,3-dichloropropane	−38.60	84.36	22.98	28.03	32.41	35.97	41.37	45.28	51.12
1,1,1,2-tetrachloroethane	−35.54	84.53	24.62	28.29	31.07	33.17	36.11	38.11	40.61
1,1,1-trichloroethane	−33.84	76.62	22.02	25.70	28.65	30.89	34.08	35.98	39.00
1,1,1-trichloropropane	−38.84	86.02	27.52	32.65	36.90	40.24	45.15	48.32	53.00
1,1,1-trichlorobutane	−43.84	95.42	33.02	39.60	45.15	49.59	56.22	60.66	67.40
1,1,1-trichloropentane	−48.84	104.82	38.52	46.55	53.40	58.94	67.29	73.00	81.60
1,1,1-trichlorohexane	−53.84	114.22	44.02	53.50	61.65	68.29	78.36	85.34	95.80
pentachloroethane	−34.00	90.95	28.27	31.86	34.47	36.70	38.62	40.03	41.03
hexachloroethane	−34.06	94.77	32.72	36.16	38.35	39.76	41.39	42.25	43.31
trichloroethylene	−1.88	77.67	19.26	21.80	23.67	25.06	26.94	28.15	29.79
tetrachloroethylene	−3.15	81.47	22.73	25.10	26.72	27.86	29.28	30.07	30.97
2-chloro-1,3-butadiene	5.56	76.07	21.99	27.15	31.32	34.67	39.57	42.20	48.03
2,3-dichloro-1,3-butadiene	−12.44	81.49	25.45	30.51	34.52	37.67	42.13	45.04	49.43
1,1,2-trichloro-1,3-butadiene	−1.39	90.73	28.16	33.23	37.15	40.15	44.19	46.67	50.38

[a] Units: $\Delta H_f°$, kcal/mol; $S°$ and C_p, cal/(mol·K).

interaction corrections on a per chlorine base. The corrections are near constant for the alkanes through four at 1.28/Cl atom, but increase rapidly above four, where number of gauche interaction increase 2-fold for each Cl added.

Contributions to entropy and heat capacities are from translation, rotations, vibrations, and internal rotations. Changes in vibration and internal rotation with increased number of Cl's will affect the interaction (correction) terms. For chloro alkenes interaction terms (groups), INT/CD/Cl_2, INT/CD/Cl_3, and INT/CD/Cl_4, have no intramolecular rotation effect. As the number of chlorines across double bond increases, some vibrational frequencies decrease and lead to increase entropy and heat capacities at low temperature. Interaction terms (groups) for chloroalkanes, INT/Cl_2, INT/Cl_3, INT/Cl_4 INT/Cl_5, and INT/

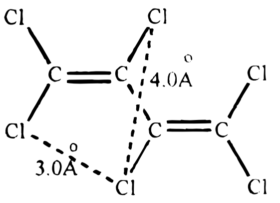
Cl$_6$, are more complex and are affected by both vibration and internal rotation. As the number of chlorines on the second carbon increase, the internal rotation barrier increases but some vibrational frequencies decrease. A combined effect results in an initial decrease and then an increase for entropies and heat capacities, with increase chlorine substitution.

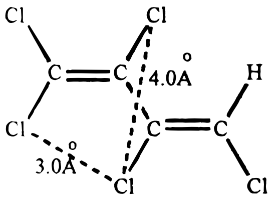
Comparison of $\Delta H_f^{\circ}{}_{,298}$ and S°_{298} data in Table 1 indicates that use of multichloro groups and interaction terms of this study provide good agreement with literature values. Deviations (group additivity values of this study vs TRC values) are less than 1.08 kcal/mol for $\Delta H_f^{\circ}{}_{,298}$. Data on entropies and heat capacities are also in good agreement with experimental data; deviations are less than 1.67 cal/(mol·K) for S°_{298} and 1.25 cal/(mol·K) for $C_p(T)$(300−1500 K).

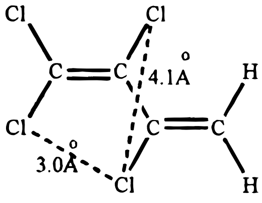
We do not know if the cis/trans energies utilized by Benson are significant relative to the Cl/Cl interactions. Calculations of these interactions at the semiempirical molecular orbital level (MOPAC 6 AM1 and PM3)[20,21] suggest very small or no difference in the thermodynamic properties of cis/trans isomers. Differences in $\Delta H_f^{\circ}{}_{,298}$ are less than 0.4 kcal/mol; S°_{298} and all heat capacity values are within 0.1 and 0.35 cal/mol·K, respectively. We term this a CIS/Cl/Cl and note that the correction is small relative to uncertainties. We therefore suggest that omission of this cis correction for simplicity is reasonable.

Estimation of Thermodynamic Properties for Larger (Greater Than C2) Chlorocarbons. An important correction in larger chlorocarbons is use of the Cl/Cl interaction term values for gauche interactions where a chlorine is gauche to a methyl that contains a Cl. For example, 1,1,2,3-tetrachloropropane would then have one INT/Cl3 for the one Cl/Cl interactions plus the one gauche-Cl interaction across the C1−C2 carbons, and one INT/Cl2 interaction for two Cl/Cl interactions across the C2−C3 carbons. Examples are provided in the estimations in Table 4. The use of gauche-Cl interaction results from comparison of our group additivity estimation with limited literature data[16] on C3 and C4 chlorocarbons and comparisons of empirically corrected MOPAC6 PM3 calculated results on larger chlorocarbon systems.

We provide a further example of chlorine−chlorine interactions and describe one additional, important, interaction term for use in unsaturated chlorocarbons. MOPAC6 PM3 and AM1 calculations suggest reasons for the comparatively high enthalpies of formation for the following chlorinated 1,3-butadienes.







The distance between Cl atoms attached to the two CD/CD/Cl carbons is about 4.0 Å, while distance between the Cl atom on the CD/CD/Cl carbons and the Cl's cis(Z) to the ethylene groups is only ca. 3.0 Å. The result of this close interaction between the two chlorines (cis-like interaction across three bonds) is to twist the CD−CD single bond so the molecule is nonplanar and the π resonance is lost. We term this a Z/Cl/CD3 interaction (group) and calculate a correction value of 18.01 kcal/mol from three molecules in the literature[16] for $\Delta H_f^{\circ}{}_{,298}$ and 0.65 cal/(mol·K) for S°_{298}.

We have derived five chlorohydrocarbon groups and 10 interaction terms from a total of 28 molecules in the literature. It is proposed that this set of groups and interaction terms be used to estimate higher carbon number chlorohydrocarbons until higher level calculations and or experimental data are available for development of an improved estimation scheme. At present limited results from an empirically derived correction applied to semiempirical calculations suggest that the accuracy of this group additivity scheme is reasonable.[20]

Summary

Three multichloro groups plus five interaction terms for chloroalkanes and two groups plus five interaction terms for chloroalkenes for use in group additivity are developed. The multichloro groups combined with the interaction groups yield an improved estimation method for thermodynamic properties (ΔH_f°, S°, and $C_p(T)$ (300−1500 K) for larger and more complex multichlorocarbon species, where no literature thermodynamic property data are available.

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