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## Estimates of Gibbs free energies of formation of chlorinated aliphatic compounds

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**Key words:** biodegradation, chlorinated compounds, Gibbs free energy of formation, group contribution method, xenobiotic

### Abstract

The Gibbs free energy of formation of chlorinated aliphatic compounds was estimated with Mavrovouniotis' group contribution method. The group contribution of chlorine was estimated from the scarce data available on chlorinated aliphatics in the literature, and found to vary somewhat according to the position of chlorine in the molecule. The resulting estimates of the Gibbs free energy of formation of chlorinated aliphatic compounds indicate that both reductive dechlorination and aerobic mineralization of these compounds can yield sufficient energy to sustain microbial growth.

### Introduction

Data on the Gibbs free energy of formation of halogenated compounds are scarce (Dean 1985). This is unfortunate because such data can be used to predict the potential of compounds to serve as an energy source for microbial growth. Mavrovouniotis (1990, 1991) recently presented an elegant group contribution method to estimate the Gibbs free energy of formation for compounds of biological interest. To this end, he evaluated the contribution of various groups to the free energy of formation of organic compounds. Unfortunately, his paper did not contain values for the contribution of chlorine substituents. In the present paper, literature data on the Gibbs free energy of formation of halogenated aliphatic compounds are summarized and used to estimate the group contribution of chlorine. The values thus obtained will be used to estimate the Gibbs free energy of formation of various halogenated acyclic compounds of biological interest.

### Materials and methods

#### *Background*

The group contribution method for the determination of the Gibbs free energy of formation of organic compounds is based on the idea that (i) a given compound is considered to be composed of groups, that (ii) numerical values can be assigned to these groups, and that (iii) adding the values of these groups to a (constant) starting value yields a reliable estimate of the compound of interest. Table 1 lists the values for the contributions of a number of open-chain groups with one or more free bonds as estimated by Mavrovouniotis (1990). Also given are the value of origin, i.e. the starting value that is used in the estimation, and a value to be used if a compound consists solely of carbon and hydrogen atoms. These values, as well as the estimates obtained with these values, are for compounds in aqueous solution at a concentration of 1 M.

The use of the group contribution method is illustrated with butyrate as an example. Butyrate can be broken down into groups in a straightforward manner. As shown in Table 2, the calculation encompasses the addition of the contributions (multiplied by the number of occurrences) of each group to the fixed contribution of origin. In this example no special corrections are needed.

### Estimation methods

Data on the Gibbs free energy of formation of halogenated aliphatic compounds have been collected in Lange's Handbook of Chemistry (1985), where they are given for the gaseous state at a partial pressure of 1 atm. Conversion of these data to values for aqueous solution proceeds via the formula

$$\Delta G_{f, \text{aq}}^{\circ} = \Delta G_{f, \text{gas}}^{\circ} + RT \ln H,$$

where  $R$  is the universal gas constant ( $8.314 \text{ J/K} \cdot \text{mol}$ ),  $T$  is the temperature (K) and  $H$  is the Henry constant in  $\text{atm} \cdot \text{l} \cdot \text{mol}^{-1}$ . Values for the Henry constant were taken from references (Leighton & Calo 1981; Mackay & Shiu 1981; Gossett 1987; Ashworth

Table 1. Contributions of groups and corrections to the standard Gibbs free energy of formation; the values are taken from Mavrovouniotis (1991).

Group or correction	Contribution kcal/mol
– CH <sub>3</sub>	7.9
> CH <sub>2</sub>	1.7
> CH –	– 4.8
> C <	– 12.8
= CH –	11.1
= CH <sub>2</sub>	18.4
= CH <	5.0
– COO <sup>–</sup>	– 72.0
– CH = O	17.8
– OH (primary)	– 29.3
– OH (secondary)	– 32.0
– OH (tertiary)	– 30.5
Origin <sup>a</sup>	– 23.6
Correction for hydrocarbon molecule <sup>b</sup>	4.0

<sup>a</sup> A contribution which must be added to every compound.

<sup>b</sup> A correction for molecules containing only C and H.

et al. 1988). The standard Gibbs free energy of formation values are listed in Table 3 where they are given for both the gaseous phase and for 1 M aqueous solutions. The Henry constants used for the conversion are also stated in Table 3.

The Gibbs free energy of formation values listed in Table 3 were used to estimate the group contribution of chlorine, as outlined below for chloropentane: the  $\Delta G_{f, \text{aq}}^{\circ}$  value for chloropentane is  $-7.1 \text{ kcal/mol}$  (Table 3), while the contribution of the non-halogen groups amounts to  $-8.9 \text{ kcal/mol}$ . Thus the contribution of Cl is estimated to be  $1.8 \text{ kcal/mol}$ . This procedure was followed to obtain estimates for the contributions of all chlorines listed in Table 3. The resulting estimates for the group contribution of chlorine in various acyclic compounds are listed in Table 4.

### Results and discussion

The group contribution of Cl to the Gibbs free energy of formation of aliphatic compounds estimated here ranges from  $-0.2$  to  $+6.5 \text{ kcal/mol Cl}$  (Table 4), while Mavrovouniotis reports that the accuracy of his group contribution method is generally better than  $2 \text{ kcal/mol}$  (Mavrovouniotis 1990, 1991). This strongly suggests that the contribution of chlorine to the Gibbs free energy of formation of aliphatic compounds is not constant, but varies with the position of the group within a molecule. A similar conclusion was drawn by Mavrovouniotis (1990, 1991) for the hydroxyl group (Table 1).

The trends revealed in Table 4 can be summarized as follows: (i) the contribution of chlorine in-

Table 2. Calculation of the Gibbs free energy of formation of butyrate according to the group contribution method.

Group or correction	Number of occurrences	Contribution kcal/mol	Total contribution kcal/mol
Origin	1	– 23.6	– 23.6
– CH <sub>3</sub>	1	7.9	7.9
– CH <sub>2</sub> –	2	1.7	3.4
– COO <sup>–</sup>	1	– 72.0	– 72.0
Total			– 84.3

Table 3. Henry's constants and standard Gibbs free energy of formation of selected chlorinated compounds at 25° C.

Compound	H <sup>a</sup>	$\Delta G_f^\circ$			
		atm.l/mol	kcal/mol		kJ/mol
			gas	aqueous	gas
Methanes					
Methane	667	− 12.15	− 8.31	− 50.79	− 34.74
Chloromethane	9.41	− 13.97	− 12.61	− 58.40	− 52.71
Dichloromethane	2.96 <sup>2b</sup>	− 16.46	− 15.82	− 68.80	− 66.11
Trichloromethane	4.21 <sup>b</sup>	− 16.76	− 15.91	− 70.06	− 66.50
Tetrachloromethane	29.5 <sup>b</sup>	− 12.80	− 10.80	− 53.50	− 45.10
Ethanes					
Ethane	501	− 7.84	− 4.17	− 32.77	− 17.43
Chloroethane	12.1 <sup>b</sup>	− 14.46	− 12.99	− 43.01	− 36.83
1,2-Dichloroethane	1.41 <sup>b</sup>	− 17.65	− 17.44	− 73.78	− 72.93
1,1-Dichloroethane	6.25 <sup>b</sup>	− 17.52	− 16.44	− 73.23	− 68.69
1,1,2-Trichloroethane	0.91 <sup>b</sup>	− 18.52	− 18.58	− 77.41	− 77.64
1,1,2,2-Tetrachloroethane	0.25 <sup>b</sup>	− 20.45	− 21.27	− 85.48	− 88.92
1,1,1-Trichloroethane	17.4 <sup>b</sup>	− 18.21	− 16.52	− 76.12	− 69.04
1,1,1,2-Tetrachloroethane	2.77	− 19.20	− 18.60	− 80.26	− 77.75
Pentachloroethane	2.18	− 16.79	− 16.33	− 70.18	− 68.26
Hexachloroethane	8.35 <sup>b</sup>	− 13.13	− 11.88	− 54.88	− 49.62
Propanes					
Propane	709	− 5.63	− 1.75	− 23.53	− 7.32
1-Chloropropane	10.9	− 12.11	− 10.70	− 50.62	− 44.73
1,2-Dichloropropane	3.56	− 19.86	− 19.11	− 83.01	− 79.88
1,3-Dichloropropane	2.38	− 19.74	− 19.23	− 82.51	− 80.38
1,2,3-Trichloropropane	0.32	− 23.37	− 24.05	− 97.69	− 100.53
Butanes					
Butane	950	− 4.10	− 0.05	− 17.14	− 0.21
1-Chlorobutane	16.6 <sup>c</sup>	− 9.27	− 7.61	− 38.75	− 31.81
2-Chlorobutane	24.1 <sup>c</sup>	− 12.78	− 10.90	− 53.42	− 45.56
Pentanes					
Pentane	1238	− 2.00	2.21	8.36	9.24
1-Chloropentane	23.6 <sup>c</sup>	− 8.94	− 7.07	− 37.37	− 29.56
Ethylenes					
Ethylene	215	16.31	19.48	68.18	81.43
Chloroethylene	27.8 <sup>d</sup>	12.31	14.27	51.46	59.65
<i>cis</i> -1,2-Dichloroethylene	4.08 <sup>d</sup>	5.82	6.65	24.33	27.80
<i>trans</i> -1,2-Dichloroethylene	9.38 <sup>d</sup>	6.35	7.67	26.54	32.06
1,1-Dichloroethylene	26.1 <sup>d</sup>	5.78	7.71	24.16	32.23
Trichloroethylene	9.58 <sup>d</sup>	4.75	6.08	19.86	25.41
Tetrachloroethylene	17.7 <sup>d</sup>	4.90	6.60	20.48	27.59

<sup>a</sup> Data from Mackay and Shiu (1981) except where indicated.<sup>b</sup> Data from Ashworth et al. (1988).<sup>c</sup> Data from Leighton and Calo (1981).<sup>d</sup> Data from Gossett (1987).

creases with the number of chlorines present on one carbon atom; (ii) the contribution of chlorine bound to a primary carbon is larger than the contribution of a chlorine bound to a secondary carbon; (iii) the contribution of chlorine bound to vicinal carbon atoms is lower than average. In view of these trends it is not justified to assign one value as 'the' estimate for the group contribution of chlorine. The observation that there are some clear trends in the contribution of chlorine enables us, however, to make an educated guess of the contribution of chlorine in various organic molecules. This is shown in Table 5 where the Gibbs free energy of formation of various chlorinated compounds has been estimated

Table 4. Estimated group contributions of chlorine.

Compound <sup>a</sup>	Contribution kcal/mol Cl
<b>Methanes</b>	
Chloromethane	3.1
Dichloromethane	3.0
Trichloromethane	4.2
Tetrachloromethane	6.4
<b>Ethanes</b>	
Chloroethane	1.0
1,2-Dichloroethane	1.4
1,1-Dichloroethane	2.0
1,1,2-Trichloroethane	2.7
1,1,2,2-Tetrachloroethane	3.0
1,1,1-Trichloroethane	4.0
1,1,1,2-Tetrachloroethane	4.0
Pentachloroethane	5.0
Hexachloroethane	6.2
<b>Propanes</b>	
1-Chloropropane	1.6
1,2-Dichloropropane	-0.2
1,3-Dichloropropane	-0.2
1,2,3-Trichloropropane	0.3
<b>Butanes</b>	
1-Chlorobutane	3.0
2-Chlorobutane	0.0
<b>Pentanes</b>	
1-Chloropentane	1.8
<b>Ethylenes</b>	
Chloroethylene	8.4
<i>cis</i> -1,2-Dichloroethylene	4.0
<i>trans</i> -1,2-Dichloroethylene	4.5
1,1-Dichloroethylene	3.9
Trichloroethylene	4.5
Tetrachloroethylene	6.3

<sup>a</sup> In aqueous solution at a concentration of 1 M.

by means of the group contribution method. The values used for the group contribution of chlorine are also indicated. These values were based on the estimates in Table 4 in combination with the assumption that the presence of a hydroxygroup will affect the contribution of a chlorine group in much the same way as the presence of a chlorine group.

Recently Helgeson (1992) used Benson's method to estimate the Gibbs free energy of formation values for chlorinated acetates. The estimates for chloroacetate (-92.86 kcal/mol) and dichloroacetate (-97.53 kcal/mol) agree well with the values for these compounds presented in Table 5. For trichloroacetate there is a difference of 5.7 kcal/mol between Helgeson's estimate (-102.14 kcal/mol) and the estimated value listed in Table 5 (-96.4 kcal/mol). Thus the two different valuation procedures give fairly similar results.

In environmental sciences, Gibbs free energy of formation data are useful to predict reaction equilibria, and to evaluate whether processes are exer-

Table 5. Estimates of Gibbs free energy of formation.

	$\Delta G_f^\circ$			
	kcal	x (kcal)	kcal	kJ
<b>Ethanol</b>				
Ethanol	-43.3		-43.3	-181.0
Chloroethanol	-49.1 + x	0.7	-48.8	-204.0
Dichloroethanol	-56.0 + 2x	2.4	-51.2	-214.0
Trichloroethanol	-64.0 + 3x	4.0	-52.0	-217.4
<b>Ethanal</b>				
Ethanal	-33.5		-33.5	-140.0
Chloroethanal	-39.7 + x	1.4	-38.3	-160.1
Dichloroethanal	-46.2 + 2x	2.4	-41.4	-173.1
Trichloroethanal	-54.2 + 3x	4.0	-42.2	-176.4
<b>Acetates</b>				
Acetate	-87.7		-87.7	-366.6
Chloroacetate	-93.3 + x	1.0	-92.3	-385.8
Dichloroacetate	-100.4 + 2x	2.0	-96.4	-403.0
Trichloroacetate	-108.4 + 3x	4.0	-96.4	-403.0
<b>Propionates</b>				
Propionate	-86.0		-86.0	-359.5
2-Chloropropionate	-92.5 + x	0.0	-92.5	-368.7
3-Chloropropionate	-92.2 + x	1.6	-90.6	-378.7
2,2-Dichloropropionate	-100.5 + 2x	1.0	-98.5	-411.7
2,3-Dichloropropionate	-98.7 + 2x	0.0	-98.7	-412.6
3,3-Dichloropropionate	-98.7 + 2x	2.0	-94.7	-395.8
3,3,3-Trichloropropionate	-106.7 + 3x	4.0	-94.7	-395.8

gonic or endergonic. The latter is especially important for evaluating the question whether a certain reaction can potentially serve as a source of metabolic energy for microorganisms which catalyze this reaction. This question can now be answered for a wide variety of halogenated compounds. Table 6 lists the Gibbs free energy values and redox potentials for the reductive dehalogenation of various classes of chlorinated aliphatic compounds with hydrogen as the electron donor. These values indicate that chlorinated compounds have redox potentials similar to the redox couple  $\text{NO}_3^-/\text{NO}_2^-$  ( $E_o' = 433$  mV) (Thauer et al. 1977). This is substantially lower than the redox potential for  $\text{O}_2$  ( $E_o' = 818$  mV) (Thauer et al. 1977), but much higher than the redox potential for the total reduction of sulfate to sulfide ( $-220$  mV) (Zehnder & Stumm 1988). Thus microorganisms in anaerobic environments can potentially benefit from the use of chlorinated aliphatic compounds as electron acceptors. A similar con-

clusion has previously been reached for halogenated aromatic compounds (Dolfing & Harrison 1992; Holmes et al. 1993). This evaluation shows that the uncertainty inherent to the group contribution method is acceptable for the above assessment, as the uncertainty of the estimates of the Gibbs free energy changes listed in Table 6 is estimated to be 5 kcal/mol or 20 kJ/reaction.

A discussion of the potential of chlorinated aliphatic compounds to serve as a source of energy via oxidative conversions is also interesting. Table 7 shows the amount of Gibbs free energy available for the mineralization of chlorinated aliphatic compounds with oxygen as the electron acceptor. Equation 1 gives the amount of energy available from the complete mineralization of n-chloroalkanes, based on estimates made according to the group contribution theory.

Table 6. Gibbs free energy values for reductive dehalogenation of selected chlorinated compounds with hydrogen as the electron donor, and calculated redox potentials of the corresponding Cl-alkyl/alkyl couples<sup>a</sup>.

Organic substrate	Organic product	$\Delta G^\circ$ kJ/reaction	$E_o'$ m V
<i>Chloroacetates</i>			
Trichloroacetate	Dichloroacetate	-171.2	473
Dichloroacetate	Chloroacetate	-154.0	384
Chloroacetate	Acetate	-152.0	374
<i>Chloropropionates</i>			
3,3,3-Trichloropropionate	3,3-Dichloropropionate	-172.4	479
3,3-Dichloropropionate	3-Chloropropionate	-154.1	384
2,3-Dichloropropionate	3-Chloropropionate	-137.3	297
2,3-Dichloropropionate	2-Chloropropionate	-127.3	246
2,2-Dichloropropionate	2-Chloropropionate	-128.2	250
3-Chloropropionate	Propionate	-152.0	374
2-Chloropropionate	Propionate	-162.0	425
<i>Chloroethanols</i>			
Trichloroethanol	Dichloroethanol	-167.8	455
Dichloroethanol	Chloroethanol	-161.2	421
Chloroethanol	Ethanol	-148.2	354
<i>Chloromethanes</i>			
Tetrachloromethane	Trichloromethane	-192.6	584
Trichloromethane	Dichloromethane	-170.8	471
Dichloromethane	Chloromethane	-157.4	402
Chloromethane	Methane	-153.2	380

<sup>a</sup> Calculated according to the relationship  $\Delta G^\circ = \sum \Delta G_f^\circ$  (products) -  $\sum \Delta G_f^\circ$  (substrates) for the reaction: organic substrate +  $\text{H}_2 \rightarrow$  organic product +  $\text{H}^+$  +  $\text{Cl}^-$ ; the  $\Delta G_f^\circ$  values for the organic compounds were taken from Table 6; other values used were  $\Delta G_f^\circ$  ( $\text{H}_2$ ) = 0;  $\Delta G_f^\circ$  ( $\text{H}^+$ ) = -39.9 kJ/mol (pH = 7);  $\Delta G_f^\circ$  ( $\text{Cl}^-$ ) = -131.3 kJ/mol. The redox potentials were calculated according to Thauer et al. (1977) with the relationship  $E_o' = (\Delta G^\circ / -0.193) - 414$ .

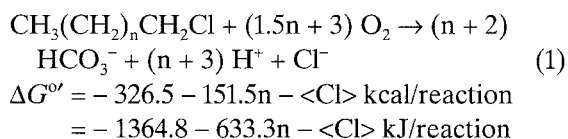
Table 7. Gibbs free energy values for the mineralization of selected chlorinated compounds and their non-chlorinated analogs with O<sub>2</sub> as the electron acceptor.

Reaction	$\Delta G^{\circ'}$ kJ
<b>Methanes</b>	
CH <sub>4</sub> + 2 O <sub>2</sub> → CO <sub>2</sub> + 2 H <sub>2</sub> O	- 826
CH <sub>3</sub> Cl + 1.5 O <sub>2</sub> → CO <sub>2</sub> + H <sub>2</sub> O + H <sup>+</sup> + Cl <sup>-</sup>	- 742
CH <sub>2</sub> Cl <sub>2</sub> + O <sub>2</sub> → CO <sub>2</sub> + 2 H <sup>+</sup> + 2 Cl <sup>-</sup>	-662
CHCl <sub>3</sub> + 0.5 O <sub>2</sub> + H <sub>2</sub> O → CO <sub>2</sub> + 3 H <sup>+</sup> + 3 Cl <sup>-</sup>	- 596
CCl <sub>4</sub> + 2 H <sub>2</sub> O → CO <sub>2</sub> + 4 H <sup>+</sup> + 4 Cl <sup>-</sup>	- 551
<b>Ethanes</b>	
Ethane + 3.5 O <sub>2</sub> → 2CO <sub>2</sub> + 3 H <sub>2</sub> O	- 1466
Chloroethane + 3 O <sub>2</sub> → 2CO <sub>2</sub> + 2 H <sub>2</sub> O + H <sup>+</sup> + Cl <sup>-</sup>	- 1381
1,1-Dichloroethane + 2.5 O <sub>2</sub> → 2CO <sub>2</sub> + H <sub>2</sub> O + 2 H <sup>+</sup> + 2 Cl <sup>-</sup>	- 1283
1,2-Dichloroethane + 2.5 O <sub>2</sub> → 2CO <sub>2</sub> + H <sub>2</sub> O + 2 H <sup>+</sup> + 2 Cl <sup>-</sup>	- 1279
1,1,1-Trichloroethane + 2 O <sub>2</sub> → 2CO <sub>2</sub> + 3 H <sup>+</sup> + 3 Cl <sup>-</sup>	- 1217
1,1,2-Trichloroethane + 2 O <sub>2</sub> → 2CO <sub>2</sub> + 3 H <sup>+</sup> + 3 Cl <sup>-</sup>	- 1210
1,1,1,2-Tetrachloroethane + 1.5 O <sub>2</sub> + H <sub>2</sub> O → 2CO <sub>2</sub> + 4 H <sup>+</sup> + 4 Cl <sup>-</sup>	- 1142
1,1,2,2-Tetrachloroethane + 1.5 O <sub>2</sub> + H <sub>2</sub> O → 2CO <sub>2</sub> + 4 H <sup>+</sup> + 4 Cl <sup>-</sup>	- 1131
Pentachloroethane + O <sub>2</sub> + 2 H <sub>2</sub> O → 2CO <sub>2</sub> + 5 H <sup>+</sup> + 5 Cl <sup>-</sup>	- 1085
Hexachloroethane + 0.5 O <sub>2</sub> + 3 H <sub>2</sub> O → 2CO <sub>2</sub> + 6 H <sup>+</sup> + 6 Cl <sup>-</sup>	- 1038
<b>Ethanols</b>	
Ethanol + 3 O <sub>2</sub> → 2CO <sub>2</sub> + H <sub>2</sub> O	- 1303
Chloroethanol + 2.5 O <sub>2</sub> → 2CO <sub>2</sub> + 2 H <sub>2</sub> O + H <sup>+</sup> + Cl <sup>-</sup>	- 1042
Dichloroethanol + 2 O <sub>2</sub> → 2CO <sub>2</sub> + H <sub>2</sub> O + 2 H <sup>+</sup> + 2 Cl <sup>-</sup>	- 795
Trichloroethanol + 1.5 O <sub>2</sub> → 2CO <sub>2</sub> + 3 H <sup>+</sup> + 3 Cl <sup>-</sup>	- 555
<b>Ethanal</b>	
Ethanal + 2.5 O <sub>2</sub> → 2CO <sub>2</sub> + 2 H <sub>2</sub> O	- 1106
Chloroethanal + 2 O <sub>2</sub> → 2CO <sub>2</sub> + H <sub>2</sub> O + H <sup>+</sup> + Cl <sup>-</sup>	- 1020
Dichloroethanal + 1.5 O <sub>2</sub> → 2CO <sub>2</sub> + 2 H <sup>+</sup> + 2 Cl <sup>-</sup>	- 941
Trichloroethanal + O <sub>2</sub> + H <sub>2</sub> O → 2CO <sub>2</sub> + 3 H <sup>+</sup> + 3 Cl <sup>-</sup>	- 872
<b>Acetates</b>	
Acetate + 2 O <sub>2</sub> → 2CO <sub>2</sub> + H <sub>2</sub> O + OH <sup>-</sup>	- 800
Chloroacetate + 1.5 O <sub>2</sub> → 2CO <sub>2</sub> + H <sub>2</sub> O + Cl <sup>-</sup>	- 715
Dichloroacetate + O <sub>2</sub> + H <sub>2</sub> O → 2CO <sub>2</sub> + H <sub>2</sub> O + H <sup>+</sup> + 2 Cl <sup>-</sup>	- 631
Trichloroacetate + 0.5 O <sub>2</sub> + 2 H <sub>2</sub> O → 2CO <sub>2</sub> + H <sub>2</sub> O + 2 H <sup>+</sup> + 3 Cl <sup>-</sup>	- 566

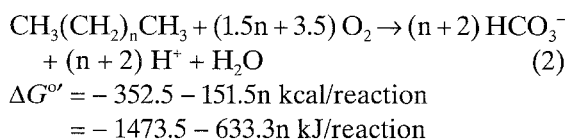
Table 8. Energetics of the first steps in the degradation pathway of 1,2-dichloroethane.

Reaction	$\Delta G^{\circ'}$ kJ
1,2-Dichloroethane + H <sub>2</sub> O → Chloroethanol + H <sup>+</sup> + Cl <sup>-</sup>	- 65.2
Chloroethanol → Chloroethanal + H <sub>2</sub>	+ 43.9
PQQ + H <sub>2</sub> → PQQH <sub>2</sub>	- 97.2 <sup>a</sup>
Chloroethanal + H <sub>2</sub> O → Chloroacetate <sup>-</sup> + H <sub>2</sub> + H <sup>+</sup>	+ 11.3
NAD <sup>+</sup> + H <sub>2</sub> → NADH + H <sup>+</sup>	- 18.1 <sup>a</sup>
Chloroacetate <sup>-</sup> + H <sub>2</sub> O → Hydroxyacetate <sup>-</sup> + H <sup>+</sup> + Cl <sup>-</sup>	- 63.0
Sum: 1,2-Dichloroethane + 3 H <sub>2</sub> O + PQQ + NAD <sup>+</sup> → Hydroxyacetate <sup>-</sup> + PQQH <sub>2</sub> + NADH + 4 H <sup>+</sup> + 2 Cl <sup>-</sup>	- 188.3 kJ

<sup>a</sup> Data from Dawson et al. (1986).



where  $\langle \text{Cl} \rangle$  stands for the group contribution of chlorine in the parent molecule. A comparison of this amount with the Gibbs free energy available from the mineralization of alkanes (equation 2) reveals that mineralization of n-chloroalkanes yields only slightly less energy than mineralization of their non-chlorinated analogs.



This trend is also visible in Table 7, and can be explained by the fact that the presence of a chlorine instead of a hydrogen group makes the molecule more oxidized and therefore decreases the number of reducing equivalents that are released when the molecule is mineralized. In the presence of oxygen, reducing equivalents represent a potential source of energy.

Knowledge of the Gibbs free energy of formation values of chlorinated compounds also allows an evaluation of the energetics of their degradation pathway, provided that the Gibbs free energy of formation values of the intermediates are also known. Table 8, for example, shows the energetics of the first steps of the degradation pathway of 1,2-dichloroethane in *Xanthobacter autotrophicus* GJ10 (Janssen et al. 1985, 1987). These values reveal that the oxidation of chloroethanol to chloroethanal and of chloroethanal to chloroacetate are highly endergonic reactions, which only proceed when coupled to reduction of electron acceptors like PQQ and NAD<sup>+</sup>.

The calculations presented in Table 8 show that both hydrolytic dechlorination steps are exergonic. The amount of energy available per step is 64 kJ/mol chloride released. There are no indications that *X. autotrophicus* GJ10 conserves this energy for growth. An alternative pathway could start with the reductive dechlorination of 1,2-dichloroethane to

chloroethane. This reaction releases 135 kJ/mol chloride, an energy yield sufficient to allow biological conservation of energy (Dolfing & Tiedje 1987; Dolfing 1990; Mohn & Tiedje 1990). It is, however, questionable whether aerobic organisms would be energetically better off by choosing this alternative route, as reductive dechlorination encompasses consumption of reducing equivalents (Dolfing & Tiedje 1986), and aerobic microorganisms can also use these reducing equivalents for the highly exergonic reduction of oxygen to H<sub>2</sub>O. The amount of energy available from the mineralization of a compound depends on the Gibbs free energy values of substrates and products, and not on the biochemical pathway taken. The pathway, in combination with the biochemical mechanisms employed by the organism that catalyzes the reactions, determines how much energy is actually conserved.

## Conclusions

The group contribution method is an acceptable method for the estimation of Gibbs free energy of formation of chlorinated aliphatic compounds. The contribution of chlorine varies somewhat with the number and position of chlorine atoms in the molecule. The accuracy of the resulting estimates is better than 5 kcal/mol (20 kJ/mol). This makes the results usable for predicting whether conversion of a chlorinated compound can serve as an energy source for microorganisms and whether certain conversion steps in a degradation pathway are exergonic or endergonic.

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