Thermochemical Database of Halomethanes, Halosilanes, Halophosphines, and Haloamines

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An accurate thermochemical database for 28 halides of carbon, silicon, nitrogen, and phosphorus is presented. The database provides improved standard enthalpies of formation for several compounds of ecological importance (CH_3F, CF_2Cl_2, $CFCl_3$) together with enthalpies of other compounds which are not known due to experimental difficulties in measuring their enthalpies. We also present a comparison of the latest ab initio methods (CBS-QB3 and G3) which are used for thermochemical predictions. The comparison shows that the G3 method consistently underestimates $\Delta H°_f$ by 1−2 kJ/mol (relative to CBS-QB3).

INTRODUCTION

The need for reliable thermochemical data often outstrips the rate at which such measurements can be performed.[1] 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 pentaatomic molecules.[2] Even the enthalpies of ecologically important halomethanes, CH_3F, CF_2Cl_2, and $CFCl_3$, are not known with high precision; the knowledge of accurate enthalpies is essential for successful modeling of processes in atmospheric chemistry.

We have used a combination of high-level ab initio methods and isodesmic reaction[3] schemes to obtain standard enthalpies of formation and thus fill the gaps in our knowledge of enthalpies and also to analyze trends in thermochemical stability along a series of related compounds. To obtain accurate enthalpies, one needs to employ a computational method which provides accurate total electronic energies (e.g. newly introduced CBS-QB3 and G3 methods which were shown to provide such energies[4,5]). Also, accurate standard enthalpies for species participating in isodesmic reactions need to be known. As reference enthalpies, we have utilized data from refs 2 and 6, which have a precision of ±2 kJ/mol.

METHOD OF CALCULATION

The ab initio calculations were performed with the Gaussian 98 set of programs,[7] which incorporates G3 and CBS-QB3 methods as a standard.

RESULTS AND DISCUSSION

The results of the calculations are presented in Tables 1−3. In addition, the tables display the most precise previously reported values[2,6,8−9] together with isodesmic reaction equations which were used in deducing enthalpies for particular compounds.

The choice of the isodesmic reaction is not unique, so those reactions were selected where accurate (the best currently available) enthalpies for compounds included in a particular reaction are known.

Many values are reported here for the first time and would be very difficult to measure experimentally due to the instability of the compounds in question (e.g. NH_2F and NHF_2).

The trends in enthalpies are of some interest. In general, the enthalpies become more negative and exothermic (i.e. the compounds become more stable thermochemically) upon increasing the number of halogen substituents. However, there are two exceptions to this trend: one in the CH_nCl_{4-n}

Table 1. $\Delta H°_f$(g,298.15K)/(kJ mol^{-1}) for Halomethanes

molecule	previous[2,6,9]	CBS-QB3	G3	isodesmic reacn
CH_4	-74.6 ± 0.3 [2]			
CF_4	-933.2 ± 0.75 [2]			
CCl_4	-96.0 [9]			
CH_3F	-234.3 [9]	-241.7	-239.3	$CH_4 + CF_4 = CH_3F + CHF_3$
CHF_3	-692.9 ± 2.0 [6]			
CH_3Cl	-83.7 [9]			
$CHCl_3$	-103.2 [9]			
CF_3Cl	-709.2 ± 2.9 [6]			
$CFCl_3$	-288.7 [9]	-289.1	-288.1	$3CF_3Cl = CFCl_3 + 2CF_4$
CH_2F_2	-450.7 [9]	-452.7	-451.0	$2CH_2F_2 = CH_4 + CF_4$
CH_2Cl_2	-95.5 [9]			
CF_2Cl_2	-491.6 [9]	-494.1	-493.8	$2CF_3Cl = CF_2Cl_2 + CF_4$
CH_2FCl	-261.9 [9]	-254.0	-254.3	$2CHF_3 + CF_3Cl = CH_2FCl + 2CF_4$
CHF_2Cl	-481.6 [9]	-477.6	-477.5	$CHF_3 + CF_3Cl = CHF_2Cl + CF_4$
$CHFCl_2$	-283.3 [9]	-278.4	-277.5	$2CF_3Cl + CHF_3 = CHFCl_2 + 2CF_4$

Table 2. $\Delta H°_f(g,298.15K)/(kJ \ mol^{-1})$ for Halosilanes

molecule	previous[2,9]	CBS-QB3	G3	isodesmic reaction
SiH_4	34.7 ± 1.5			
SiF_4	-1615.0 ± 0.8			
$SiCl_4$	-662.2 ± 0.8			
SiH_3F	-376.6	-354.8	-353.2	$3SiH_4 + SiF_4 = 4SiH_3F$
$SiHF_3$	-1200.8	-1200.7	-1199.1	$SiH_4 + 3SiF_4 = 4SiHF_3$
SiH_3Cl	-141.8	-133.6	-132.8	$3SiH_4 + SiCl_4 = 4SiH_3Cl$
$SiHCl_3$	-496.2	-489.6	-488.2	$SiH_4 + 3SiCl_4 = 4SiHCl_3$
SiF_3Cl	-1318.0	-1372.3	-1373.2	$3SiF_4 + SiCl_4 = 4SiF_3Cl$
$SiFCl_3$	-841.0	-895.3	-895.8	$SiF_4 + 3SiCl_4 = 4SiFCl_3$
SiH_2F_2	-790.8	-773.3	-770.7	$SiH_4 + SiF_4 = 2SiH_2F_2$
SiH_2Cl_2	-320.5	-310.9	-309.4	$SiH_4 + SiCl_4 = 2SiH_2Cl_2$
SiF_2Cl_2		-1131.9	-1133.2	$SiF_4 + SiCl_4 = 2SiF_2Cl_2$
SiH_2FCl		-538.8	-537.1	$2SiH_4 + SiF_4 + SiCl_4 = 4SiH_2FCl$
$SiHF_2Cl$		-958.5	-957.8	$SiH_4 + 2SiF_4 + SiCl_4 = 4SiHF_2Cl$
$SiHFCl_2$		-721.3	-720.6	$SiH_4 + SiF_4 + 2SiCl_4 = 4SiHFCl_2$

Table 3. $\Delta H°_f(g,298.15K)/(kJ \ mol^{-1})$ for Haloamines and Halophosphines[a]

molecule	previous[8,9]	CBS-QB3	G3	isodesmic reaction
NH_3	-45.9 ± 0.4			
NF_3	-132.1			
NH_2F	-20.9	-26.9	-26.4	$2NH_3 + NF_3 = 3NH_2F$
NHF_2	-65.3	-61.2	-60.3	$NH_3 + 2NF_3 = 3NHF_2$
PH_3	$22.9 \ ^9$			
PF_3	-958.4			
PCl_3	-288.7			
PH_2F		-246.0	-245.0	$2PH_3 + PF_3 = 3PH_2F$
PHF_2		-575.3	-573.9	$PH_3 + 2PF_3 = 3PHF_2$
$PHFCl$		-365.8	-364.6	$PH_3 + PF_3 + PCl_3 = 3PHFCl$
PH_2Cl		-61.8	-60.5	$2PH_3 + PCl_3 = 3PH_2Cl$
$PHCl_2$		-168.3	-166.5	$PH_3 + 2PCl_3 = 3PHCl_2$
PF_2Cl		-722.4	-723.6	$2PF_3 + PCl_3 = 3PF_2Cl$
$PFCl_2$		-499.0	-500.3	$PF_3 + 2PCl_3 = 3PFCl_2$

[a] N.B. The enthalpy of PH_3 was taken from ref 9, instead of the traditional value of 5.4.

series and the other in the NH_nF_{3-n} series. In the CH_nCl_{4-n} series CCl_4 has an enthalpy comparable to that of CH_2Cl_2. The explanation suggested by Mingos[10] is that crowding of four large chlorine atoms in CCl_4 around a small central carbon reduces the relative stability of CCl_4 in comparison with e.g. $CHCl_3$. The suggestion is corroborated by the fact that no such anomalies were observed in the CH_nF_{4-n} series (which has smaller F ligands) or in the halosilane series (which has a larger silicon atom in the center). The anomaly in the NH_nF_{3-n} series is reflected in the fact that both NH_2F and NHF_2 have enthalpies comparable to or smaller than the enthalpy of NH_3. A plausible rationalization can be found in the fact that NH_2F and NHF_2 can decompose into thermochemically more stable products: N_2 and HF.

One can consider the energy (enthalpy) stabilization (gain) upon sequential replacement of hydrogen by a halogen (Table 4). The data show that (taking into consideration the exceptions discussed above) the gains are not linear, although they generally increase with the degree of halogenation. The replacement of the first hydrogen generates less stabilization than replacement of the last halogen. This result represents a caveat against using simple bond energies in calculating enthalpies. Furthermore, the rate of stabilization tends to level-off with the degree of halogenation in fluoromethanes, fluorosilanes, and chlorosilanes. For instance, replacement of the third and fourth hydrogens in fluromethanes brings the same stabilization (240 kJ/mol). On the other hand the replacement of the first hydrogen leads to substantially smaller stabilization (167 kJ/mol).

Table 4. Enthalpy Stabilization (kJ/mol) Achieved by Subsequent Hydrogen/Halogen Replacement along a Particular Series (Negative Values Indicate Stabilization, Positive Destabilization)

CH_4	CH_3F	CH_2F_2	CHF_3	CF_4
	-167.1	-210.5	-240.7	-240.3
SiH_4	SiH_3F	SiH_2F_2	$SiHF_3$	SiF_4
	-410.9	-414.2	-410.0	-414.1
CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
	-7.3	-13.1	-10.9	13.7
SiH_4	SiH_3Cl	SiH_2Cl_2	$SiHCl_3$	$SiCl_4$
	-176.1	-178.7	-175.7	-166.5
NH_3	NH_2F	NHF_3	NF_3	
	19.5	-33.9	-71.8	
PH_3	PH_2F	PHF_2	PF_3	
	-267.9	-328.9	-384.5	
PH_3	PH_2Cl	$PHCl_2$	PCl_3	
	-83.4	-106.0	-122.2	

Another point of interest in this work concerns comparison of the performance of CBS-QB3 and G3 methods in thermochemical calculations. The data in Tables 1−3 clearly indicate that the G3 method gives enthalpies which are 1−2 kJ/mol less stable than those obtained with the CBS-QB3 method. However, since 1−2 kJ/mol is well within the "chemical accuracy" of 1 kcal/mol, both methods appear to be equally suitable for thermochemistry.

REFERENCES AND NOTES

(1) Irikura, K. K. In *Energetics of Stable Molecules and Reactive Intermediates*; Minas da Piedade, M. E., Ed.; Kluwer: Dordrecht, The Netherlands, 1999; p 353.
(2) Gurvich, L. V.; Veyts, I. V.; Alcock, C. B. *Thermodynamic Properties of Individual Substances*, Vol.2, Part I; Hemisphere: New York, 1991.

(3) Ponomarev, D. A.; Takhistov, V. V. *J. Chem. Educ.* **1997**, *74*, 201.

(4) Montgomery, J. A.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110*, 2822.

(5) Curtiss, L. A.; Raghavachari, K.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

(6) Ruščić, B.; Michael, J. V.; Redfern, P. C.; Curtiss, L. A.; Raghavachari, K. *J. Phys. Chem. A* **1998**, *102*, 10889.

(7) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(8) Baumgärtel, H.; Jochims, H.-W.; Rühl, E.; Bock, H.; Dammel, R.; Minkwitz, J.; Nass, R. *Inorg. Chem.* **1989**, *28*, 943.

(9) Chase, M. W. NIST-JANAF Thermochemical Tables, 4th ed., Monograph 9. *J. Phys. Chem. Ref. Data* **1998**, 1−1951.

(10) Mingos, D. M. P. *Essential Trends in Inorganic Chemistry*; Oxford University Press: Oxford, U.K., 1998.

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