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Theoretical Calculations of Thermodynamic Properties of Small Halogen-Containing Molecules: Assessment of Reliability

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With emphasis on enthalpies of formation, the reliability of recent all-valence-electron MNDO SCF-MO calculations with complete geometry optimisation have been assessed by comparison of computed and experimental values for selected halogen containing compounds.

INTRODUCTION

Very recently we reported[1] an experimental value for the enthalpy of formation of nitrogen triiodidemonoammine $\Delta H_f^\circ NI_3NH_3,c$, 298.15. From this, confident estimates of the (I-N) bond energy and of the gas-phase value ΔH_f° NI_3,g, 298.15 may be made. Comparison of the latter, essentially experimental quantity, with values calculated using published computational procedures[2] revealed some serious discrepancies. Since there are available reliable experimental values of enthalpies of formation for several other small halogen-containing molecules of Groups III and V we have collated these in order to assess the success of the increasingly popular current computational procedures by comparison with experimental values. The value of a reliable computational method to determine standard enthalpies of formation of species inaccessible by experiment is very great.

METHODS

Computation

Since the required basis sets of the *ab initio* method do not yet exist for heavy elements such as iodine, we restrict our calculations to the use of MNDO (modified neglect of differential overlap) semi-empirical molecular orbital method due to Dewar and Thiel[2]. Preliminary calculations were carried out using the AM1 (Austin Model 1) method[3], but later the new PM3 Hamiltonian[4] became available for testing. The methods and molecules used for parameterisation of the various elements are given in the following references: nitrogen[5], boron[6], phosphorus[7], fluorine[8], chlorine[9], bromine[10], and iodine[11].

The MNDO method takes into account the directionality of the atomic orbitals used in the LCAO approximation when calculating the repulsion integrals; the main weakness lies in the tendency to overestimate repulsion

between atoms when they are at the van der Waals' distance apart. The AM1 method obviates the problem by using additional Gaussian terms in the core repulsion functions. The PM3 method differs from AM1 only in the values of the atomic parameters for 12 different elements. Complete geometry optimisation was allowed.

Experimental

Detailed descriptions of experimental procedures may be found in the appropriate references. In these laboratories values of ΔH_f°, c, 298.15 of PI_3, P_2I_4[12], BI_3[13], and NI_3NH_3 were obtained using isoperibol reaction calorimetry, and values of ΔH_{vap}°, c → g, 298.15 for PI_3 and P_2I_4 were found[12] using the Knudsen effusion method.

NI_3, g, cannot be isolated, due to its extreme instability. Hence a value for $\Delta H_f^\circ NI_3$, g, 298.15 was estimated using the following cycle.

$$\begin{array}{ccc} NI_3NH_3,c & \xrightarrow{\Delta H_{vap}^\circ} & NH_3NI_3,\ g \\ \Delta H_f^\circ \uparrow & & \downarrow \Delta H_D \\ N_2,g + 3/2H_2,g + 3/2I_2,c & \longrightarrow & NI_3,\ g + NH_3,g \end{array}$$

ΔH_{vap}° is estimated as 63 kJ mol^{-1} by comparison with the experimental values for BI_3,PI_3,I_2 and P_2I_4, which show surprisingly little variation ($\simeq 58 < \Delta H_{vap}^\circ < \simeq 69$, kJ mol^{-1}).

ΔH_D° is a dissociation term which is identified as of hydrogen bond character. Such bonds lie in the range 19 to 40 kJ mol^{-1}; we accordingly ascribe a value of 29 kJ mol^{-1}.

Since values of $\Delta H_f^\circ NI_3NH_3$,c, and of NH_3,g, are well established, we calculate $\Delta H_f^\circ NI_3$,g, 298.15 = 288 kJ mol^{-1}. Confidence limits are difficult to assess in view of the assumptions above, but are most unlikely to be of sufficient magnitude to affect the comparison with computed values.

RESULTS AND DISCUSSION

In this section we compare computed and experimental values of enthalpies of formation of gaseous fluorine, nitrogen and iodine, and then of gas-phase molecules of formula AX_3 (A = B,N,P; X = F,Cl,Br,I). Finally, we comment on bond lengths, structure and dipole moments.

TABLE 1
COMPARISON OF EXPERIMENTAL AND COMPUTED VALUES OF ΔH_f°,g/kJ mol^{-1}

	Computed (MNDO) AM1	PM3	Experimental	Δ
F_2	+31	+31	0.0	+31
N_2	+37	+37	0.0	+37
I_2	+90	+90	+62	+28

(Δ : computed—experimental)

Clearly both computational methods give the same results which are consistently 32 ± 5 kJ mol^{-1} less stable than the experimental (or defined) values. Possibly this arises from the use of compounds containing polar bonds for the parameterisation and hence results in an under-estimation of the strength of the purely covalent bonds in the diatomic elements. Since the error is the same for all three elements it presumably does not arise from an over-estimation of the lone pair—lone pair repulsion terms as these are different for each of the three species. If one allows for this error, then the sublimation enthalpy of solid iodine is computed correctly.

TABLE 2

COMPARISON OF EXPERIMENTAL AND COMPUTED VALUES OF $\Delta H_f^\ominus$,g/kJ mol^{-1} OF SOME HALIDES OF BORON, NITROGEN, PHOSPHORUS

	Computed (MNDO) AM1	PM3	Experimental	Δ
BF_3	−772	−1092	−1137	+45
BI_3	−21	+39	+25	+14
NF_3	−167	−142	−126	−16
NCl_3	+229	+189		
NBr_3	+348	+208		
NI_3	+393	+289	+288	+1
PF_3		−959	−919	−60
PCl_3		−403	−287	−116
PBr_3		−159	−139	−20
PI_3		+106	+5	+101

(Δ = Computed (PM3) value—experimental value).

Results for the halides of the first short period elements, boron and nitrogen, derived using the PM3 Hamiltonian, are clearly superior to those derived from the AM1 procedure, which is therefore not considered further. The excellent result for NI_3 and the encouraging value for NF_3 lend credence to the computed values for NCl_3 and NBr_3. Interestingly a value for $\Delta H_f^\ominus NCl_3$,liq = + 230 has been quoted[14]; the origin is obscure and is presumably not experimental. Experimental measurements on NCl_3 and NBr_3, even in condensed states, are most unlikely in view of their extreme sensitivities.

The results obtained for the second short period element, phosphorus, are most disappointing, not only in the absolute values, but in differences. Although *d*-orbital contributions are implicity covered in these

semi-empirical methods, it is not unusual for greater deviations to occur than with first row elements, where such contributions are of little significance. Clearly the present (PM3) approach has no value for second row elements as far as standard enthalpies of formation are concerned.

However, it is interesting to exploit the possibility of computing additional information (e.g. structures, ionisation potentials, dipole moments, bond orders, eigen-values and eigen-vectors). Some of these are collated in Table 3.

TABLE 3

CALCULATED AND EXPERIMENTAL DIPOLE MOMENTS AND BOND LENGTHS FOR NITROGEN AND PHOSPHORUS HALIDES

	Dipole moment		Bond length	
	Computed	Expt.[15]	Computed	Expt.[16]
NF_3	0.20	0.23	1.315	1.36
NCl_3	0.654	0.6	1.735	1.75
NBr_3	1.268		1.816	
NI_3	0.004		1.943	2.20†
PF_3	2.44	1.03	1.556	1.54
PCl_3	1.38	0.80	1.989	2.03
PBr_3	0.48	0.58	2.088	
PI_3	1.82		2.262	

†$NI_3.NH_3$,c, complex.

Again, the calculated values for the phosphorus trihalides seem unreliable, but those for nitrogen triflluoride and trichloride give good agreement with experiment. However, the calculations suggest that NI_3 in the gas phase is close to planar in structure. The structure of $NI_3.NH_3$ complex in the solid state is close to pyramidal ($I—\hat{N}—I = 110^9 \pm 1.5°$).[17]

CONCLUSION

At the time of writing it is clear that useful quantities may be computed for simple halides of first row elements, but that extension to elements of higher atomic number is dangerous. The superiority of the PM3 to the AM1 application is considerable. Presumably further improvements will be made, either via parameterisation or through development of the more fundamental *ab initio* method.

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