MNDO-Estimations of the Standard Heat of Formation of Some Binary Sulfur–Nitrogen Compounds and their Derivatives

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Introduction

The area of the chemistry of binary compounds composed of sulfur and nitrogen has become a very active field of research in the last two decades [1]. Despite a wide range of research activities virtually no thermodynamic data are available for this class of materials, the exception being a single report of a value for the standard heat of formation of tetrasulfur tetranitride [2]. Since our laboratory has been concerned with theoretical studies of these materials for a number of years [3], we have put together in tabular form estimates of the standard enthalpy of formation, ΔH_f° for most of the known compounds of this class. We have included a few materials which are presently unknown, (*e.g.*, N_2S, $S_4N_4^{2-}$, and S_2N_2 open chain) but whose existence may be considered probable, as reflected by the known chemistry of these materials [4].

Calculation and Results

The enthalpies of formation have been calculated by the MNDO method of Dewar *et al.* [5] using the Restricted Hartree–Fock approximation. Open shell systems have been calculated using an Unrestricted Hartree–Fock wave function [6]. The results are given in Table I.

The MNDO method when applied to sulfur–nitrogen compounds has been shown to predict molecular geometries that agree with the experimental structures in the cases of disulfur dinitride, S_2N_2 (D_{2h} ground state) [7], tetrasulfur tetranitride, S_4N_4 [8], the pentasulfur pentanitrogen cation, $S_5N_5^+$ [9] and the $S_3N_3^-$, the trisulfur trinitrogen cation [3]. In general, the MNDO calculated enthalpies of formation tend to be somewhat more negative than the corresponding experimental values for carbon containing compounds and the same is probably true for sulfur–nitrogen compounds as well. Nevertheless, in an absolute sense the values calculated are comparable in accuracy to those obtainable from minimal basis set, single determinant SCF calculations [10]. More importantly the values calculated *relative to each other* are probably reliable. Thus in the Table we indicate the enthalpy of formation of the materials listed relative to the enthalpy of formation of S_4N_4. It is somewhat difficult to assign absolute error estimates for the calculated heats of formation, but we estimate the values to be accurate to about 10%.

The unstable nature of these materials (note all the calculated ΔH_f°'s are positive) makes the experimental calorimetric measurement of heats of reaction for these materials difficult. The lack of knowledge of heat capacity data additionally complicates the experimental problem. Simple combustion calorimetry is complicated by the formation of gaseous products, *i.e.*, SO_3 and NO_2 and should probably be carried out in the presence of water to enable the formation of nitric and sulfuric acids. Until these problems are resolved it is hoped that these MNDO estimates of the standard enthalpies of formation will serve some useful purpose.

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TABLE I. Thermodynamic Data for Various Sulfur Nitrogen Compounds.

Compound	ΔH_f° (Kcal/mol)	I.P. (ev)	ΔH_f°/relative†	Dipole Moment††
SNN	47.6	10.4	0.237	1.57
NSN	212	10.6	1.05	1.69
S_2N_2	118	10.9	0.587	0.01
S_2N_2 chain	147*	–	0.731	2.74
	142**	–	0.706	2.48
$S_2N_2^{2+}$	771	25.1	3.84	–
$S_2N_2^{2-}$	174	–4.6	0.866	–
$S_2N_3^{1+}$	300	18.2	1.49	–
$S_3N_2^{1+}$	309	12.0	1.54	–
$S_3N_2^{2+}$	661	23.4	3.29	–
$S_3N_3^{1-}$	84	3.6	0.418	–
$S_3N_3^{1+}$	370	15.1	1.84	–
1,2 S_4N_2	43.7	10.8	0.217	1.67
1,3 S_4N_2	104	9.9	0.517	2.04
1,4 S_4N_2	113	9.8	0.562	1.02
$S_4N_3^{1+}$	351	14.6	1.75	–
S_4N_4	201	9.4	1.00	5.52
$S_4N_4H_4$	66.5	10.1	0.331	1.54
$S_4N_4^{2+}$	674	19.8	3.35	–
$S_4N_4^{2-}$	190	–1.6	0.945	–
$S_4N_5^{1+}$	389	14.5	1.93	–
$S_4N_5^{1-}$	244	4.7	1.21	–
$S_5N_5^{1+}$	434	12.9	2.16	–
$S_5N_5^{1+}$ (heart)	434	12.9	2.16	–
(azulene)	434	12.9	2.16	–

†The standard enthalpy of formation relative to ΔH_f° for S_4N_4. ††Units Debyes. *(singlet state). **(triplet state).

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