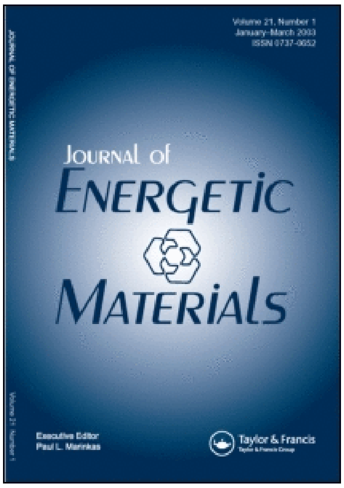

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CALCULATIONS OF HEATS OF FORMATION
FOR NITRAMINES AND ALKYL NITRATES WITH PM3 AND MM2

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ABSTRACT

We have calculated heats of formation (ΔH_f°) for nitramines and alkyl nitrates with the semi-empirical molecular orbital theory, PM3 and the molecular mechanics, MM2. Both methods can estimate ΔH_f° accurately. By combining heats of vaporization and sublimation obtained by the additivity rule with ΔH_f° in the gas phase obtained by PM3 and MM2, ΔH_f° in condensed phases can be estimated accurately enough for energy hazards prediction.

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INTRODUCTION

In order to investigate characteristics of energetic materials, their heats of formation (ΔH_f°) are indispensable. We had attempted to calculate ΔH_f° for various aromatic and aliphatic nitro compounds with the semi-empirical molecular orbital theory and the molecular mechanics, and showed their capability for ΔH_f° estimation[1-3]. Here, we have calculated ΔH_f° for various nitramines and alkyl nitrates. In addition, we have attempted to estimate ΔH_f° in condensed phases by using heats of vaporization and sublimation obtained by the additivity rule.

METHOD

The programs used were MOPAC(Molecular Orbital Package) version 5.01[4] and MM2(Molecular Mechanics version 2)[5]. We employed MM2 parameters for the nitramines which Lauderdale et al.[6] had decided. For alkyl nitrates, we used MM2 parameters of the carbonyl group to supplement insufficient ones. Calculations were conducted on HITAC M-682H and M-880 in the Computer Centre of the University of Tokyo.

RESULTS AND DISCUSSION

Structure

About the MM2 parameters of nitramines, Landerdale et al.[6] evaluated them using observed structures of several nitramines. They were 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), N,N-dimethylnitramide (DMN) and 1,1,3,5-tetranitrohexahydropyrimidine (DNNC). The performance of their parameters is shown in the reference.

Wang et al.[7] had decided MM2(85) parameters for nitrates and calculated structures and ΔH_f° for several nitrates. But their parameters showed not so good performance to MM2(77). So we tentatively adapted parameters for the carbonyl group. Calculated and observed[8] geometries of CH_3ONO_2 are shown in Table 1. Fairly good values have been obtained with three methods.

TABLE 1

Geometries of Methyl Nitrate Calculated with PM3 and MM2

Method	C-O (A)	O-N (A)	N-O(av.) (A)	∠ C-O-N (degree)	∠ O-N-O(av.) (degree)
obs.[8]	1.437	1.402	1.207	112.7	115.3
MM2	1.419	1.436	1.230	116.3	120.1
PM3	1.508	1.495	1.224	118.1	123.8
6-31G[9]	1.464	1.361	1.213	116.8	116.2

Gas-phase Heat of Formation

Gas-phase heats of formation at 298K have been calculated for aliphatic nitramines and alkyl nitrates with PM3 and MM2. Results are summarized in Tables 2-3. As the MM2 bond enthalpy of N-NO2 group had not been decided, we assigned 11.1 kcal to it from observed ΔH_f° of RDX, HMX and DMN. Similarly, for O-NO2 group, we assigned 14 kcal from observed ΔH_f° of methyl nitrate and nitroglycerin.

Both methods can estimate ΔH_f° accurately. That is, ΔH_f° are calculated within ± 8 kcal/mol from the observed values by PM3 and MM2.

TABLE 2

Calculated Heats of Formation for Nitramines

Compound	ΔH_f°(kcal/mol) PM3	MM2	obs.	ref.
DMN*	1.3	0.9	-0.2	(10)
RDX*	40.8	42.8	46.8	(11)
HMX*	59.3	57.8	56.4	(11)
1,4-dinitropiperazine	17.1	21.1	13.9	(12)
N,N-diethylnitramide	-4.6	-10.7	-12.7	(12)

*:compounds used to determine MM2 parameters

TABLE 3

Calculated Heats of Formation for Alkyl Nitrates

Compound	ΔH_f°(kcal/mol)		
	PM3[13]	MM2	obs.[10]
methyl nitrate*	-32.4	-26.6	-29.1
ethyl nitrate	-36.4	-34.8	-36.8
n-propyl nitrate	-41.6	-40.7	-41.6
i-propyl nitrate	-42.1	-44.7	-45.6
nitroglycerin*	-71.4	-68.7	-64.7
pentaerythritoltetranitrate	-98.3	-96.0	-92.5

*:compounds used to determine MM2 parameters

Condensed-phase Heat of Formation

Various kinds of methods had been developed to estimate ΔH_f° in the condensed state[15-17]. We have also attempted to estimate ΔH_f° of nitro compounds in condensed phases by combining heats of vaporization(Δ Hv) and heats of sublimation(Δ Hs) obtained by the additivity rule with ΔH_f° in gas phase obtained by PM3 and MM2[3]. We used Laidler's values for Δ Hv[18] and Bondi's values for Δ Hs[19]. Estimated ΔH_f° of nitramines in the solid phase are shown in Table 4. The uncertainty is within 10 kcal/mol except for

1,1,1,3,5,5,5-heptanitro-3-azapentane. This is the case with spatially crowded nitro groups discussed earlier[3]. This discrepancy reflects the limitation of the parameters used here[6].

TABLE 4

Calculated Heats of Formation for Nitramines in Solid Phase

Compound	ΔH_f^o(kcal/mol)			
	PM3	MM2	obs.	ref.
DMN	-12.4	-12.8	-16.9	(10)
RDX	8.7	10.7	14.7	(14)
HMX	16.5	15.0	17.9	(14)
DNNC	0.4	-4.3	2.0	(15)
1,4-dinitropiperazine	-9.4	-5.4	-12.7	(12)
2,2,4,6,6-pentanitro-4-azaheptane	-55.9	-62.3	-55.4	(12)
1,1,1,3,5,5,5-heptanitro-3-azapentane	-0.4	7.6	-6.7	(12)
1,3,3,5,7,7-hexanitro-1,5-diazaoctane	4.3	3.4	-5.0	(15)

About alkyl nitrates, their Δ Hv can be estimated accurately with Laidler's method[18]. Therefore, ΔH_f° in the liquid phase can be easily obtained from ΔH_f° in the gas phase. For example, calculated ΔH_f° of nitroglycol in the liquid phase were -62.6 kcal/mol by MM2 and -66.7 kcal/mol by PM3, while observed ΔH_f° was -58.0 kcal/mol. These results show that ΔH_f° calculated with PM3 and MM2 are accurate enough for using the estimation of heats of reaction for energetic materials.

CONCLUSIONS

Heats of formation for aliphatic nitramines and alkyl nitrates have been calculated with the semi-empirical molecular orbital theory and the molecular mechanics. PM3, semi-empirical MO method, and MM2, molecular mechanics, can estimate ΔH_f° within ± 8 kcal/mol of the observed values. ΔH_f° in the solid and liquid phases can be estimated within ± 10 kcal/mol of the observed values by using heats of phase change calculated with the additivity rule, except for some polynitro compounds. This method would be accurate enough to estimate energy hazards of nitramines and nitrates.

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