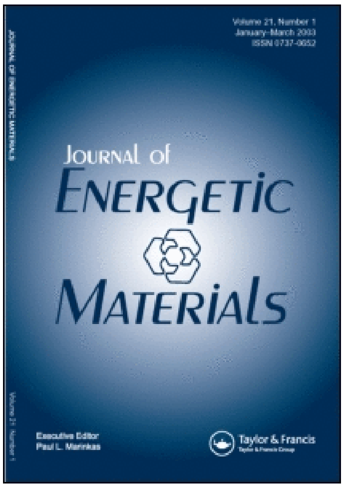

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Calculations of heats of formation for nitroalkanes with PM3 and MM2'

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CALCULATIONS OF HEATS OF FORMATION
FOR NITROALKANES WITH PM3 AND MM2'

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ABSTRACT

We have attempted to calculate heats of formation (ΔH_f°) for aliphatic nitro compounds with the semi-empirical molecular orbital theory, PM3 and the molecular mechanics, MM2'. Both methods can estimate ΔH_f° accurately, though in case of polynitro compounds, differences between observed and calculated values become slightly larger. By combining heats of vaporization and sublimation obtained by the additivity rule with ΔH_f° in gas phase obtained by PM3 and MM2', ΔH_f° in condensed phase can be estimated with accuracy enough to use ΔH_f° for energy hazards prediction.

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INTRODUCTION

In order to investigate characteristics of energetic materials, it should be indispensable to obtain their heats of formation(ΔH_f°) because heats of decomposition and heats of reaction can be calculated with ΔH_f°. We attempted to calculate ΔH_f° for several nitro compounds with the semi-empirical molecular orbital theory and the molecular mechanics, and showed their capability for ΔH_f° estimation[1]. Detailed investigation about aromatic nitro compounds has been also done[2]. Here, we calculate ΔH_f° for various nitro aliphatic compounds with the semi-empirical molecular orbital theory and the molecular mechanics. In addition, we attempt to estimate ΔH_f° in condensed phase by using heats of vaporization and sublimation obtained by the additivity rule.

METHOD

The programs used were MOPAC(Molecular Orbital Package) version 5.01[3] and MM2'(Molecular Mechanics version 2)[4]. We employed parameters for the nitro group which Tanabe et al.[5] had decided. For the parameters they have not determined, we used similar ones in MM2. All calculations were conducted on a HITAC M-682H in the Computer Centre of the University of Tokyo.

RESULTS AND DISCUSSION

Gas-phase heats of formation at 298K are calculated for aliphatic nitro compounds with PM3 and MM2'. Results are summarized in Table 1 with observed values[6]. Both methods can estimate ΔH_f° accurately. When ΔH_f° are expressed by cal/g, ΔH_f° are calculated within ± 60 cal/g from the observed values with PM3 and MM2' except for some polynitro compounds. For trinitroethane and trinitropropane, ΔH_f° estimated with MM2' are much larger than observed ones. For trinitromethane, the difference is not so large. This discrepancy reflects the limitation of the parameters used here. When we change the dipole parameter of C-N bond from 0.2 to 0, then ΔH_f° for trinitroethane and trinitropropane are -7.6 and -10.9 kcal/mol, though dipole moments become slightly smaller. For tetranitromethane, ΔH_f° estimated with PM3 and MM2' are much different from observed ones. This may be the worst case with spatially crowded nitro groups.

Cardozo[7] developed a method based on the additivity rule to estimate enthalpies of combustion, formation, vaporization and sublimation of organics. Bourasseau[8] had estimated ΔH_f° in the condensed state for various kinds of non-aromatic polynitro compounds. His method consisted of the estimation of enthalpy of formation in gaseous state, the estimation of heat of vaporization(ΔHv) and sublimation(ΔHs), and the

TABLE 1

Calculated Heats of Formation for Nitro Alkanes

Compound	ΔH_f°(kcal/mol)		
	PM3[6]	MM2[7]	obs.[6]
nitromethane	-15.9	-18.3	-17.9
nitroethane	-20.9	-24.5	-23.5
1-nitropropane	-26.8	-30.3	-30.0
2-nitropropane	-27.1	-29.8	-33.2
1-nitrobutane	-32.1	-36.2	-34.4
2-nitrobutane	-31.9	-35.5	-39.1
dinitrotomethane	-11.9	-12.4	-13.3
trinitromethane	-4.7	1.5	-3.2
tetranitromethane	6.4	30.4	18.5
1,1-dinitroethane	-17.4	-17.8	-24.1
1,2-dinitroethane	-19.6	-25.6	-22.9
1,1,1-trinitroethane	-10.0	-0.8	-12.4
1,1-dinitropropane	-22.0	-22.5	-25.9
1,3-dinitropropane	-26.6	-32.7	-31.6
2,2-dinitropropane	-23.0	-21.6	-27.0
1,1,1-trinitropropane	-8.1	-4.1	-18.4
1,1-dinitrobutane	-27.2	-28.3	-34.1
1,4-dinitrobutane	-32.7	-40.8	-38.9

calculation of interaction terms. Their methods both gave good results. Here, we also attempt to estimate ΔH_f° in condensed phase by combining Δ Hv and Δ Hs obtained by additivity rule with ΔH_f° in gas phase obtained by PM3 and MM2'. Hwang et al.[9] decided group contribution values for enthalpies of phase change of aromatic nitro compounds. The uncertainty of their method is within 15 cal/g. We used Laider's values for Δ Hv[10] and Bondi's values for Δ Hs[11]. Estimated ΔH_f° in condensed phase are shown in Tables 2-3. The uncertainty is within a few kcal/mol. It shows that ΔH_f° calculated with PM3 and MM2' are accurate enough for using the estimation of heats of reaction for energetic materials. The reason for the discrepancy of ΔH_f° for 2-methyl-2,3,3-trinitrobutane and -pentane is the same as Bourasseau's discussion[8], that is, large errors in the experimental values.

Steric energies of 1,2-dinitroethane, 1,3-dinitropropane and 1,4-dinitrobutane are 6.2, 5.2 and 3.2 kcal/mol, respectively. Bourasseau's interaction terms of nitro groups for Δ 1-2, Δ 1-3 and Δ 1-4 C-C are 5, 4 and 2 kcal/mol[8]. Considering that the steric energy of nitromethane is 0.8 kcal/mol, this result means that interaction terms in Bourasseau's calculation correspond to the steric energy in MM2.

TABLE 2

Calculated Heats of Formation for Nitro Alkanes in Liquid Phase

Compound	ΔH_f°(kcal/mol)			
	PM3	MM2'	obs.	ref.
1-nitrobutane	-43.9	-48.0	-46.0	(12)
2-nitrobutane	-43.6	-47.2	-49.6	(12)
dinitromethane	-27.0	-27.5	-25.1	(12)
1,1-dinitroethane	-33.5	-33.9	-34.7	(13)
1,1-dinitropropane	-39.2	-39.7	-40.1	(12)
1,3-dinitropropane	-43.8	-49.9	-53.5	(12)
1,1,1-trinitropropane	-31.9	-27.9	-28.1	(13)
1,1,1,4-tetranitrobutane	-46.8	-45.9	-42.8	(14)
2,2,3,3-tetranitrobutane	-33.2	-33.5	-40.1	(14)

TABLE 3

Calculated Heats of Formation for Nitro Alkanes in Solid Phase

Compound	ΔH_f°(kcal/mol)			
	PM3	MM2'	obs.	ref.
1,2-dinitroethane	-41.8	-47.8	-42.0	(12)
2,2-dinitropropane	-46.7	-45.3	-44.9	(12)
1,1,1-trinitroethane	-22.8	-12.8	-27.5	(13)
2,2-dimethyl-1,3-dinitropropane	-60.4	-75.4	-66.4	(13)
2-methyl-2,3,3-trinitrobutane	-54.3	-57.6	-79.2	(12)
2-methyl-2,3,3-trinitropentane	-58.1	-63.1	-69.4	(12)
1,1,1,4-tetranitrobutane	-40.2	-39.3	-45.3	(14)
2,2,3,3-tetranitrobutane	-45.0	-45.3	-43.5	(14)

CONCLUSION

Heats of formation for aliphatic nitro compounds 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 ± 60 cal/g of the observed value except for some polynitro compounds. ΔH_f° in solid and liquid phase can be estimated within a few kcal/mol of observed values by using heats of phase change calculated with the additivity rule. It would be accurate enough to estimate energy hazards of aliphatic nitro compounds.

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