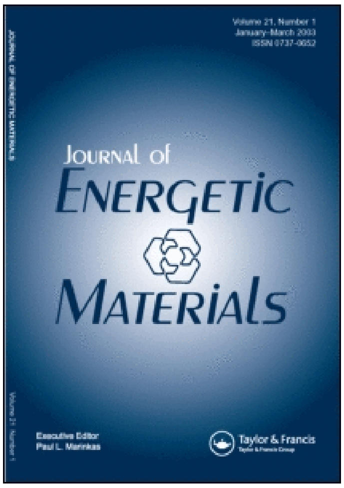

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Estimation of Δ$_f$ of nitro derivatives of benzene and toluene using AM1 and DSC

Dong-Rong Hwang[a]; Masamitsu Tamura[a]; Tadao Yoshida[a]; Nariaki Tanaka[b]; Fumio Hosoya[c]
[a] Department of Reaction Chemistry, Faculty of Engineering, University of Tokyo, Bunkyo-ku, Tokyo, Japan [b] Process Technologe Laboratory, Sumitomo Chemical Co. Ltd., Niihama-shi, Japan [c] Technology Development Center, Hosoya Kako Co. Ltd., Akikawa-shi, Japan

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ESTIMATION OF ΔH°_f OF NITRO DERIVATIVES OF BENZENE AND TOLUENE USING AM1 AND DSC

Dong-Rong Hwang, Masamitsu Tamura
and Tadao Yoshida
Department of Reaction Chemistry ,
Faculty of Engineering , University of Tokyo,
Bunkyo-ku, Tokyo 113, Japan

Nariaki Tanaka
Process Technologe Laboratory,
Sumitomo Chemical Co. Ltd.,
5-1 Sobiraki-cho, Niihama-shi 792, Japan

Fumio Hosoya
Technology Development Center,
Hosoya Kako Co. Ltd.,
Osawa, Sugao, Akikawa-shi 197, Japan

ABSTRACT

The AM1 molecular orbital method and reduced pressure differential scanning calorimetry(RP-DSC) were applied to nitro derivatives of benzene and toluene for estimating $\Delta H^\circ_f(l)$ and $\Delta H^\circ_f(c)$. The heats of phase change were determined by RP-DSC with moderate accuracy and the combination of the heats and $\Delta H^\circ_f(g)$ estimated by AM1 gave ΔH°_f in condensed phases which are similar to those found in literatures.

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INTRODUCTION

The standard enthalpy of formation (ΔH°_f) of energetic materials is an important property for evaluating explosion heat and other explosive properties.

Though ΔH°_f of an energetic material can be obtained by measuring the heat of combustion[1], it is not feasible to do it with high accuracy. One of the methods for estimating ΔH°_f is using a group additivity rule[2,3,4]. However, many ΔH°_f of groups contained in energetic compounds have not been established.

Molecular orbital methods can in principle calculate $\Delta H^\circ_f(g)$ of any compound which is composed of atoms for which parameters have been determined. Molecular orbital calculations of energetic compounds have been carried out by Arai et al.[5], Carper et al.[6], and Davis et al.[7], using MINDO/3[8], MNDO[9] and AM1[10] methods. We applied the MNDO and AM1 to nitrogen containing compounds such as nitro compounds, nitrate esters and so on[11], and it was found that for these compounds the AM1 is more suitable than the MNDO, and by applying an empirical correction $\Delta H^\circ_f(g)$ can be estimated accurately.

A molecular orbital method calculates ΔH°_f in vapor phase, but not those in condensed phases. Most energetic compounds are in condensed phases at room temperature. Therefore ,in order to estimate precisely ΔH°_f of energetic compounds under the ordinary conditions, it is required.to correct for heats of evaporation or sublimation. The methods for determining heats of vaporization and sublimation were compiled by J.D.Cox and G.Pilcher[1]. The heats of energetic compounds were determined by Cundall et al.[12], and Hara et al.[13],using the Knudsen cell and DTA, respectively. These are methods for measuring vapor-pressure-temperature relations.

We have measured heats of phase change by calorimetry using reduced pressure differential scanning calorimetry (RP-DSC) and showed that the determination of heats of melting, vaporization and sublimation are possible by this method[14].

Here we describe the results of applying the RP-DSC to nitro derivatives of benzene and toluene and of combining RP-DSC data and AM1 calculations to estimate ΔH°_{f} of the nitro compounds in condensed phase.

EXPERIMENTAL

Materials

Nitro compounds used here are of reagent grade and some of them were recrystallized for purification.

Sample Cell with a Pin Hole

Aluminium sample cells were made by Seiko Densi Kogyo Co. Ltd. and a 0.1 mm pin hole was perforated through the lid of the cell.

Instrument

Shimazu DSC Model 41 and attached reduced pressure apparatus were used for measuring heats of phase change of the nitro compounds. As the DSC sensor head deteriorates easily by oxidizing or corrosive gas, the exhaust line of N_2 gas was modified in order to prevent exposure of calorimetric sensors to the vapor of nitro compounds.

Procedure

(i) 2-3 mg sample of a nitro compound is weighed accurately in the Al cell, and the lid with a 0.1 mm pin hole is put on it and sealed by the sealer.

(ii) A cell with sample and a reference cell with α-Al_2O_3 are put on the cell holder and the lid of the holder is closed.

(iii) Electric source of the DSC is switched on and the heating rate is set for 20C°/min.

(iv) Flow of N_2 gas is adjusted to 10 ml/min or 40 ml/min, a vacuum pump is on, and the pressure of the cell holder is adjusted to 10 mmHg or 290mmHg.

(v) By analyzing the DSC curve using a computer, DSC extrapolated on-set temperature (Tv(DSC) or Tm(DSC)) and DSC heat (ΔHv(DSC)or ΔHm(DSC)) of the phase change of the nitro compound. For a solid compound, DSC sublimation heat (ΔHs(DSC)) is obtained as follows:

$$\Delta Hs(DSC) = \Delta Hm(DSC) + \Delta Hv(DSC)$$

AM1 Calculation

The AM1 calculation and correction for nitro groups were carried out using the same procedures as previous paper[11], that is,a standard geometry is input from the CHEMOGRAM by Yoneda[15], the geometry is optimized by MOPAC program[16], and obtained $\Delta H°_f$ is corrected for number (n) of nitro groups in a benzene ring.

$$\Delta H°_f(AM1,corr) = \Delta H°_f(AM1,opt) - 9.5\ n$$

RESULTS AND DISCUSSION

Results of Experiments and Calculations

Results of DSC experiments and AM1 calculations, and relevant literature values are listed in Table 1.

TABLE 1

Results of RP-DSC Experiments and AM1 Calculations, and Relevant Literature Values for Nitro Compounds

compound	ΔH_m (kcal/mol)	T_m (°C)	ΔH_v (kcal/mol)	T_v (°C)	ΔH_s (kcal/mol)	ΔH_f° (kcal/mol) $\Delta H_f^\circ(c)$	$\Delta H_f^\circ(l)$	$\Delta H_f^\circ(g)$	ΔH_f°(AM1,corr) (kcal/mol)
Benzene	2.35^b	5.7^b	8.09^a	25^b	---	$10.13^{a,b}$	11.72^a	19.81^a	22.0^d
Nitrobenzene	2.8^b	6^b	10.9^d 11.4^b	165.3^d	---	0.2^b	3.6^b	16.1^b	15.8^d
1,2-Dinitrobenzene	5.3^d	114.5^d	15.3^d	213.6^d	20.6^d	-0.4^b	$4.9^{b,d}$	$20.2^{b,d}$	22.5^d
1,3-Dinitrobenzene	4.2^d	86.9^d	15.8^d	160^d	20.0^d 19.4^e	-8.1^a	-3.9^a	11.3^a	14.2^d
1,4-Dinitrobenzene	6.3^d	171^d	16.2^d	$162.4^{*,d}$	22.5^d	-9.2^b	$-2.9^{b,d}$	$13.3^{b,d}$	14.3^d
1,3,5-trinitrobenzene	3.8^d	121^d	19.1^d	210^d	22.9^d 23.8^b	-8.9^b	-5.1^b	14.9^b	16.6^c
Toluene	1.58^b	-95^b	9.08^a	110^b	---	$1.33^{a,b}$	2.91^a	11.99^a	14.4^d
o-Nitrotoluene	---	---	11.4^d	174.3^d	---		-2.3^b	$9.3^{b,c}$	9.5^d
m-Nitrotoluene	---	---	11.6^d	187.8^d	---		-7.5^b	$4.1^{b,d}$	8.1^d
p-Nitrotoluene	4.4^d	48.7^d	13.6^d	108.3^d	18.0^d 18.9^b	-11.5^b	$-7.3^{b,d}$	7.4^b	7.7^d
2,3-Dinitrotoluene	4.2^d	56.6^d	16.8^d	171^d	21.0^d				
2,4-Dinitrotoluene	5.3^d 4.8^e	67.6^d	16.5^d 15.6^e	170.4^d	21.8^d	-17.10^a	$-11.8^{a,d}$	$4.7^{a,d}$	7.3^d
2,6-Dinitrotoluene	5.7^d	54.3^d	16.1^d	155.6^d	21.8^d	-12.22^a	$-6.5^{a,d}$	$9.6^{a,d}$	11.2^d
3,4-Dinitrotoluene	4.5^d	56.3^d	16.3^d	189^d	20.8^d	------	-----	----	11.6^d
2,4,6-Trinitrotoluene	5.6^d	79^d	19.5^d 22.9^b	202^d 127^b	25.1^d 28.3^e	-16.03^a	$-10.43^{a,d}$	12.3^a	13.0^c

a) ref. 1 b) THE CHEMICAL SOCIETY OF JAPAN ,"Kagakubenran, Kisohen", Maruzen, II-221 (1984) c) ref. 11

d) this work e) ref. 13 * sublimated temperature (10 mmHg)

Comparison of DSC and Literature Values of Heats of Phase Change

Plots of ΔHm, ΔHv and ΔHs by DSC measurement against those in literatures were plotted in Figure 1. The heats of phase change measured by DSC were similar to those in literature which had been determined previously by other methods. TNT is the one for which the DSC and literature value differed greatly. The difference between observed and literature values of ΔHs is 3.2 kcal/mol (14.1 cal/g) for TNT. This difference is not large for hazard and performance evaluations of the compound. The reason for discrepancy is not clear at the moment.

Comparison of ΔH°_f Obtained from AM1-DSC and Literatures

By combining ΔH°_f(AM1,corr) and ΔHv(DSC) or ΔHs(DSC), we can get ΔH°_f of a compound in condensed phase (ΔH°_f (AM1-DSC)).

$$\Delta H^\circ_f(\text{AM1-DSC}) = \Delta H^\circ_f(\text{AM1,corr}) + Hv(\text{DSC}) \text{ or } \Delta Hs(\text{DSC})$$

ΔH°_f(AM1-DSC) and literature values are listed in Table 2. The differences between ΔH°_f(AM1-DSC) and literature values were 3-29 cal/g . Among 11 data, the differences were below 10 cal/g for 4 compounds, between 10-20 cal/g for 6, and between 20-30 cal/g for 1. The average difference was 13 cal/g and this is accurate enough for use in evaluating explosion hazards and performances of nitro compounds.

The differences between ΔH°_f(AM1-DSC) and literature values are independent of the number of nitro groups attached to one benzene ring. Therefore we can use the following empirical correction:

$$\Delta H^\circ_f(\text{ADC}) = \Delta H^\circ_f(\text{AM1-DSC}) - 0.013\, M$$

Here, ΔH°_f(ADC) is the ΔH°_f which is obtained by correcting ΔH°_f(AM1-DSC) with molecular weight M, empirically. Obtained ΔH°_f(ADC) are listed in Table 2

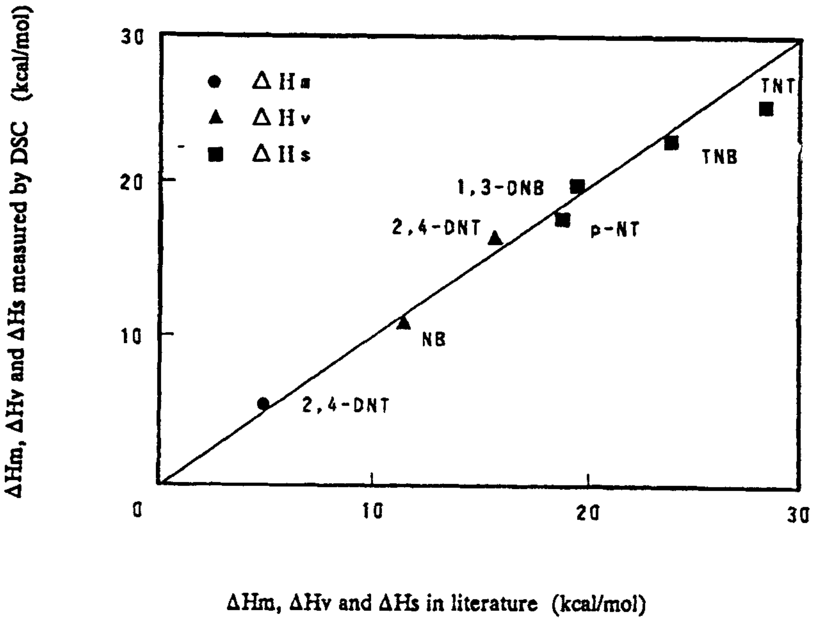

FIGURE 1

Plots of ΔHm(●), ΔHv(▲) and ΔHs(■)

Measured by DSC vs. ΔH(reference)

TABLE 2

Comparison of ΔH_f° Obtained from AM1-DSC, Corrected AM1-DSC, Group Contributions and Literatures

compounds	Phase	ΔH_f°(ref.) kcal/mol	ΔH_f°(AM1-DSC) kcal/mol	devi. cal/g	ΔH_f°(ADC) kcal/mol	devi. cal/g	ΔH_f°(AR) kcal/mol	devi. cal/g
Nitrobenzene	l	3.6^{b}	4.9	11	3.3	-2	4.0	3
1,2-Dinitrobenzene	c	-0.4^{b}	1.9	14	-0.3	1	-0.3	1
1,3-Dinitrobenzene	c	-8.1^{a}	-5.8	14	-8.0	1	-8.6	-3
1,4-Dinitrobenzene	c	-9.2^{b}	-8.2	6	-10.4	-7	-8.6	4
1,3,5-TNB	c	-8.9^{b}	-6.3	12	-9.1	-1	-9.0	-1
o-Nitrotoluene	l	-2.3^{b}	-1.9	3	-3.7	-10	-3.2	-7
m-Nitrotoluene	l	-7.5^{b}	-3.5	29	-5.3	16	-7.0	4
p-Nitrotoluene	c	-11.5^{b}	-10.3	9	-12.1	4	-11.2	2
2,4-Dinitrotoluene	c	-17.1^{a}	-14.5	14	-16.9	1	-17.1	0
2,6-Dinitrotoluene	c	-12.2^{a}	-10.6	9	-13.0	-4	-13.9	-9
3,4-Dinitrotoluene	c	---	-9.2	--	---	--	12.0	--
2,4,6-TNT	c	-16.0^{a}	-12.1	17	-15.1	4	-14.3	7
sum of absolute value of deviation				138		51		41

also.

Group Contributions of Aromatic Nitrocompounds in Gas, Liquid and Solid Phases

From the results of the present study and literature values, ΔH°_f of nitro deriatives of toluene and benzene in all phases were obtained. Then we calculated group contributions ΔH°_f of relevant groups in every phase. Results are listed in Table 3. Here, $[C_B\text{-}(NO_2)]$(mono), $[C_B\text{-}(NO_2)]$(di) and $[C_B\text{-}(NO_2)]$(tri) show ΔH°_f group contributions of mono, di and tri nitro compounds, respectively. $[\text{ORTHO}(NO_2,NO_2)]$ represents the ortho effect between two neighboring nitro groups. $[\text{ORTHO}(NO_2,CH_3,NO_2)]$(di) shows the buttress effect of two nitro groups which are in two ortho positions to the methyl group of toluene derivatives. $[C_B\text{-}(CH_3)]$ used here was obtained from the data of nitrobenzenes and nitrotoluenes, and so is only applicable to aromatic nitro compounds. By examining the contents of Table 3, it was found that $[C_B\text{-}(NO_2)]$ for mono and dinitro compounds were similar, and that for trinitro compounds was different from the other two nitro derivatives. Therefore we adopted two $[C_B\text{-}(NO_2)]$:

$$[C_B\text{-}(NO_2)](\text{MD}) = \{[C_B\text{-}(NO_2)](\text{mono}) + [C_B\text{-}(NO_2)](\text{di})\} / 2$$

$$[C_B\text{-}(NO_2)](\text{T}) = [C_B\text{-}(NO_2)](\text{tri})$$

The other effects of methyl and nitro groups were not so different from the numbers of nitro groups and ortho positions. Therefore, we used average values for the ortho effect between methyl and nitro groups:

$$\begin{aligned}[\text{ORTHO}(CH_3,NO_2)] = \{ & [\text{ORTHO}(CH_3,NO_2)](\text{mono}) \\ & + [\text{ORTHO}(CH_3,NO_2)](\text{di}) \\ & + [\text{ORTHO}(NO_2,CH_3,NO_2)](\text{di}) \\ & + [\text{ORTHO}(NO_2,CH_3,NO_2)](\text{tri}) \} / 4\end{aligned}$$

TABLE 3

Group Contributions ΔH_f° of Aromatic Nitrocompounds in Every Phase (kcal/group)

	$\Delta H_f^\circ(c)$	$\Delta H_f^\circ(l)$	$\Delta H_f^\circ(g)$	ΔH_m	ΔH_v	ΔH_s
$[C_B-(H)]$	1.56	1.95	3.30	0.40	1.35	1.74
$[C_B-(NO_2)]$(mono)	-7.6	-6.17	-1.51	1.43	4.66	6.09
$[C_B-(NO_2)]$(di)	-7.45	-5.86	-0.95	1.59	4.91	6.50
$[C_B-(NO_2)]$(tri)	-4.6	-3.65	1.67	0.95	5.32	6.27
$[C_B-(CH_3)]$	-10.1	-9.04	-5.95	1.06	3.09	4.15
[ORTHO(NO_2,NO_2)]	8.3	9.4	10.0	1.1	0.6	1.7
[ORTHO(CH_3,NO_2)](mono)	—	5.1	3.6	—	-1.5	—
[ORTHO(CH_3,NO_2)](di)	3.2	3.1	2.7	-0.1	-0.4	-0.5
[ORTHO(NO_2,CH_3,NO_2)](di)	4.1	4.2	3.8	0.1	-0.4	-0.3
[ORTHO(NO_2,CH_3,NO_2)](tri)	2.3	2.9	3.3	0.6	0.4	1.0

TABLE 4

Settled Group Contributions ΔH_f° (kcal/group)

	$\Delta H_f^\circ(c)$	$\Delta H_f^\circ(l)$	$\Delta H_f^\circ(g)$	ΔH_m	ΔH_v	ΔH_s
$[C_B-(H)]$	1.6	2.0	3.3	0.4	1.3	1.7
$[C_B-(NO_2)]$(MD)	-7.5	-6.0	-1.2	1.5	4.8	6.3
$[C_B-(NO_2)]$(T)	-4.6	-3.7	1.7	0.9	5.4	6.3
$[C_B-(CH_3)]$	-10.1	-9.0	-6.0	1.1	3.0	4.1
[ORTHO(NO_2,NO_2)]	8.3	9.4	10.0	1.1	0.6	1.7
[ORTHO(CH_3,NO_2)]	3.2	3.8	3.4	0.6	-0.4	0.2

By putting in order the above results, Table 4 is obtained.

Comparison of ΔH°_f(AM1-DSC), ΔH°_f(ADC) and ΔH°_f(AR)

The ΔH°_f of nitro benzenes and toluenes in condensed phase obtained from AM1, DSC correction and the additivity rule is listed in Table 2 along with corresponding literature values. Here , ΔH°_f(AR) are ΔH°_f which are obtained from calculation by the additivity rule using group contributions of ΔH°_f listed in Table 4. It is seen that the differences between ΔH°_f(ADC) and the literature values are within ± 20 cal/g and those between ΔH°_f(AR) and literature values are within ± 10 cal/g.

Examination of DSC Measurement of Phase Changes

Only sublimation heat can be measured for p-dinitrobenzene at 10 mmHg because peaks of melting and evaporation overlap each other. In order to determine both the heats of melting and evaporation, the pressure of reducing pressure apparatus was set up 290 mmHg. Sublimation temperature (162°C) at 10 mmHg is lower than the melting point (171°C) at 290 mmHg. An example of DSC curves are shown in Fig. 2. In Fig. 2-(a) only one peak is seen at 10 mmHg and this is a sublimation curve. The area between the peak and a line A B corresponds to the sublimation heat 22.5 kcal/mol. In Fig. 2-(b), two peaks are observed at 290 mmHg. The area between the first peak and a base line A'C corresponds to the melting heat of 6.3 kcal/mol, and that between two peaks and a base line A'B' corresponds to the sublimation heat of 22.2 kcal/mol which is very similar to 22.5 kcal/mol obtained in Fig. 2-(a).

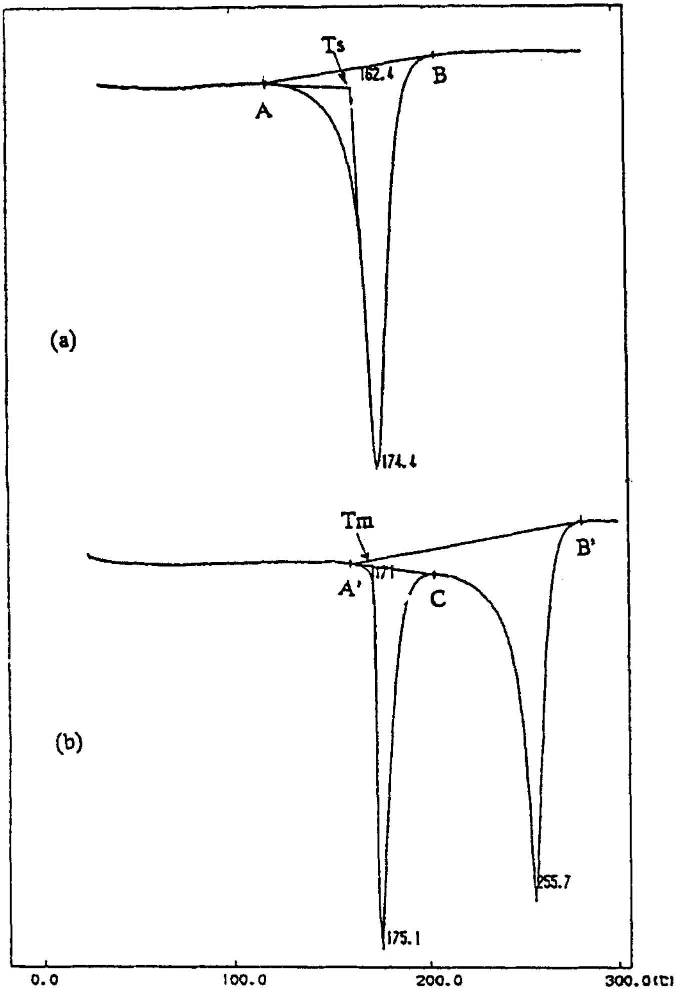

FIGURE 2

DSC Curve of p-Dinitrobenzene

Fig. 2(a) is the Curve Measured at 10 mmHg. Ts is the Extrapolated Sublimation Temperature. The Area of Base Line AB corresponds to ΔHs of 22.5 kcal/mol. Fig. 2(b) is the Curve Measured at 290 mmHg. Tm is the Extrapolated Melting Point. The Area of Base Line A'B' corresponds to ΔHs of 22.2 kcal/mol.

CONCLUSION

DSC measurement and AM1 MO calculation were combined to give high accuracy estimation of $\Delta H°_f$ of aromatic nitrocompounds in condensed phase. Furthermore, by this method, unknown group contributions of $\Delta H°_f$ were estimated. The reliabilities of both methods were within 20 cal/g and good enough to assess the safety and performance of energetic materials.

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