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Thermochemistry of nitro compounds. Experimental standard enthalpies of formation and improved group-additivity values

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Abstract

The standard molar enthalpies of vaporization $\Delta_{vap}H^0$ or sublimation $\Delta_{sub}H^0$ of 1-nitropentane A, nitrocyclohexane B, 2,4,4-trimethyl-2-nitropentane C, 3-nitro-3-(*p*-nitrophenyl)-pentane D, 1,4-dinitrobenzene E, 1,2-dinitrobenzene F, and 2-amino-nitrobenzene G were obtained from the temperature variation of the vapour pressure measured in a flow system. The standard enthalpies of formation Δ_fH^0 (l or cr) at the temperature T=298.15 K were measured using combustion calorimetry for compounds B, C and D. The derived ideal-gas enthalpies of formation of the compounds of A–G and the data available from the literature were used for the calculation of group-additivity parameters useful in the application of the Benson correlation. © 1997 Elsevier Science B.V.

Keywords: Enthalpy of formation; Enthalpy of sublimation; Enthalpy of vaporization; Group-additivity correlation; Nitro compound

1. Introduction

A number of methods for the estimation of thermochemical properties of organic compounds have been developed in recent years [1–3]. The importance of reliable experimental basis for such methods is universally accepted among both scientists and engineers. The thermochemistry of nitro compounds has not been so intensively studied as that of other homologous series. Group-additivity values for nitro compounds in a different manner were listed in [1,4,5]. Because of the scarce basis of experimental data, the number of additive parameters were derived only from one or two compounds. For example, a term of a tertiary carbon atom attached to the nitro-group has been evaluated only from the data for 2-nitropropane and 2-nitrobutane [5]. A term of a quaternary carbon atom attached to the nitro group has been derived only from the data for 2-methyl-2-nitropropane [5]. These parameters have to be checked for their validity. The results of investigation of thermochemical properties of the 1-nitropentane A, nitrocyclohexane B, 2,4,4-tri-methyl-2-nitropentane C, and 3-nitro-3-(*p*-nitrophenyl)-pentane D aimed to provide the additional thermochemical results at improvement of the Benson group-contribution correlation.

Non-nearest neighbour interactions (e.g. *ortho*, *para*, and *cis* effects) is an area in which data are insufficient to draw definitive conclusions, because in

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[1] The experimental part of the work was done at the Institute of Organic Chemistry and Biochemistry, University of Freiburg, Germany.

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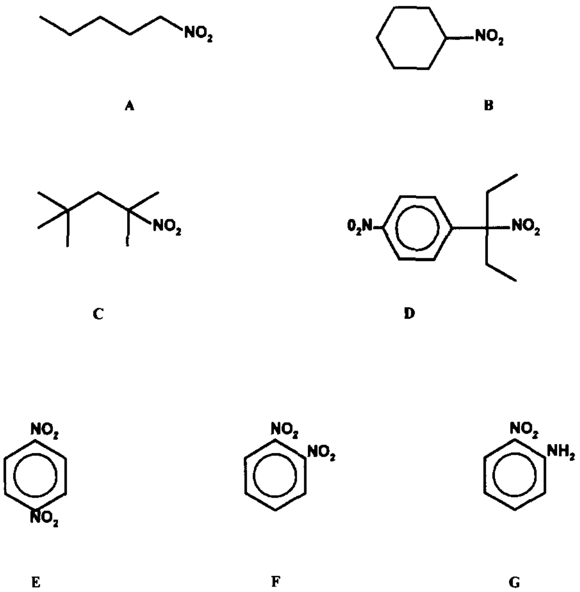

Fig. 1. Molecules of interest: A=1-nitropentane, B=nitrocyclohexane, C=2,4,4-trimethyl-2-nitropentane, D=3-nitro-3-(p-nitrophenyl)-pentane, E=1,4-dinitrobenzene, F=1,2-dinitrobenzene, and G=2-amino-nitrobenzene.

many cases thermochemical data are scarce or even contradictory. There are numerous instances with significant discrepancies among the reported measurements, hence in this work we have measured the enthalpies of sublimation of 1,4-dinitrobenzene E, 1,2-dinitrobenzene F, and 2-amino-nitrobenzene G using the transpiration method in order to clarify the discrepancies in thermochemical data of these compounds. Derived effects of *ortho* and *para* interactions of nitro and amino groups on the benzene ring were aimed to provide the correction terms for the prediction of enthalpies of formation of nitro compounds.

This paper reports thermochemical measurements (transpiration, combustion calorimetry, and DSC) leading to the standard molar enthalpies of formation in the gaseous state $\Delta_f H^0(g)$ at the temperature $T = 298.15$ K of nitro compounds A to G (Fig. 1).

2. Experimental

Samples of 1-nitropentane (A), nitrocyclohexane (B), 1,4-dinitrobenzene (E), 1,2-dinitrobenzene (F), and 2-amino-nitrobenzene (G) were commercially available from Aldrich and Merck. The samples of 2,4,4-trimethyl-2-nitropentane (C), 3-nitro-3-(*p*-nitrophenyl)-pentane (D) were synthesized in the research group of Prof. Dr C. Rüchardt at the University of Freiburg [6].

The liquid compounds were purified by repeated distillation under 1.6 KPa reduced pressure. To avoid traces of water in samples for the combustion experiments, the purified liquid samples were dried over molecular sieves and distilled once more before the combustions. Such a procedure provided colourless material, and the absence of water was verified by Karl Fischer titration. Solid samples having a mass-fraction purity about 0.99 were purified by repeated recrystallization from ethanol and petroleum ether. The sample of D was then further sublimed in vacuum directly before combustion in order to avoid any traces of solvent. The determination of purity was carried out by g.c. (sensitivity $\geq$0.01%). The purity of the samples for the combustion experiments is listed in Table 1. In samples of the 2,4,4-trimethyl-2-nitropentane C used for the combustion and transpiration experiments about 0.12 mass% of unidentified impurities (very close to the main peak) were detected by g.c.. The purity of samples for the transpiration experiments was as greater than mass fraction 0.99.

All compounds were handled under an inert atmosphere (N_2), without day light exposure and using carefully dried solvents. We used the following equipment – GC: Carlo Erba Fraktometer Vega Series GC 6000, Hewlett–Packard Integrator 3390A, N_2-flow 0.333 $cm^3 s^{-1}$, SE-30 capillary column of length 25 m. The standard temperature program: 313 K for 180 s, followed by a rate of 0.167 K s^{-1} up to 523 K. DSC, Perkin–Elmer DSC-2C.

For the measurements of the enthalpies of combustion of compounds B, C and F an isoperibolic macrocalorimeter with stirred water bath was used. The substances were filled in polythene ampoules or pressed into pellets of mass (ca. 500 mg) and were burned in oxygen at a pressure 3.04 MPa. The completeness of combustion of the crystalline sample was insured by addition of about 50 mg oil to the tablet. To ensure equilibrium in the final state, 0.78 g of water was added to the bomb. The combustion products were examined for carbon monoxide (Draeger tube) and unburnt carbon but neither was detected. The correc-

Table 1
Physical properties of the materials used in the present study

	Purity (%)	$\rho_{(293\ \mathrm{K})}$ [a] ($\mathrm{g\ cm^{-3}}$)	$c_{p(298.15\ \mathrm{K})}$ [b] ($\mathrm{J\ K^{-1}\ g^{-1}}$)	$10^{-6}(\delta V/\delta T)_p$ [c] ($\mathrm{dm^3\ K^{-1}}$)
Nitrocyclohexane	99.99	1.061	2.00	1.0
2,4,4-Trimethyl-2-nitropentane	99.88	0.918	1.46	1.0
3-Nitro-3-(*p*-nitrophenyl)-pentane	99.99	1.110	1.72	0.1
Oil [d]		0.880	0.84	1.0
Cotton [e]		1.500	1.67	0.1
Polyethene [f]		0.920	2.53	0.1

[a] Measured with pycnometer.
[b] From DSC-measurements.
[c] Estimated.
[d] $CH_{1.940}$, $\Delta_c u^0_{(\mathrm{oil})} = (-46003.6 \pm 4.0)\ \mathrm{J\ g^{-1}}$.
[e] $CH_{1.774}O_{0.887}$, $\Delta_c u^0_{(\mathrm{cotton})} = (-16945.2 \pm 4.2)\ \mathrm{J\ g^{-1}}$.
[f] $CH_{1.930}$, $\Delta_c u^0_{(\mathrm{polyethene})} = (-46361.0 \pm 3.1)\ \mathrm{J\ g^{-1}}$.

tions for nitric acid formation were based on the titration with 0.1 mol $\mathrm{dm^{-3}}$ NaOH (aq). The detailed procedure has been previously described [7]. The energy equivalent of the calorimeter was determinated with a standard reference sample of benzoic acid (sample SRM 39i, NIST). From six experiments $\varepsilon_{\mathrm{calor}}=(25112.6\pm1.9)\ \mathrm{J\ K^{-1}}$ was measured. For the reduction of the data to standard conditions conventional procedures were used [8]. The atomic weights used were those recommended by the IUPAC Commission [9](a). The density of solid compound D was determined by submerging a tablet of the substance in water in a calibrated 10 $\mathrm{cm^3}$ pycnometer. The density of the liquid nitrocyclohexene was taken from Aldrich catalog. The density of the compound C was measured in a calibrated 10 $\mathrm{cm^3}$ pycnometer. The massic heat capacities c_p and the enthalpy of fusion $\Delta_{\mathrm{fus}}H^0=(20.29\pm0.21)\ \mathrm{kJ\ mol^{-1}}$ of compound D were measured by DSC. The summary of auxiliary quantities for the combustion experiments (all auxiliary combustion energies are from own measurements) and information necessary for reducing apparent mass to real mass is given in Table 1.

The enthalpies of vaporization of compounds A–D and enthalpies of sublimation of compound E–G were determined with the method of transference in a saturated N_2-stream [7,10,11] using Clausius–Clapeyron equation. About 0.5 g of the sample was mixed with glass beads and placed in a thermostated U-tube of 20 cm length and 0.5 cm diameter. At constant temperature (±0.1 K), a nitrogen stream was passed through the U-tube and the transported amount of material was condensed in a cooled trap. The flow region 0.28–0.56 $\mathrm{cm^3\ s^{-1}}$ of the nitrogen stream was optimal in order to reach the equilibrium of saturation of transportating gas by each temperature of the investigation. The amount of condensed product was determined by g.c. analysis using an internal standard (hydrocarbons $C_{11}H_{24}$ or $C_{13}H_{28}$). The vapour pressure p at the saturation temperature was calculated from the amount of product collected within a definite time, corrected for the residual vapour pressure at condensation temperature. The latter was calculated from the linear correlation between $\ln[\{m/m^0\}/\{V(N_2)/V^0\}]$ against T^{-1} obtained by iteration. The molar enthalpies of vaporization or sublimation were calculated from the slope of this linear correlation:

$$\Delta_{\mathrm{vap}}H^0 = -R\{\mathrm{d}\ln[\{m/m^0\}/\{V(N_2)/V^0\}]\mathrm{d}T^{-1}\}$$

(with R being the ideal gas constant; m, the mass of transported compound; m^0=1 mg; $V(N_2)$, the volume of transportating gas; V^0=1 $\mathrm{dm^3}$; T=temperature). The observed enthalpies of vaporization $\Delta_{\mathrm{vap}}H^0(T)$ or sublimation $\Delta_{\mathrm{sub}}H^0(T)$ at the temperature T obtained by this procedure are listed in Table 2. Their error bars were calculated by the method of least squares of the linear correlation.

3. Results and discussion

The results for a typical combustion experiment on each compound are given in Table 3. The individual

Table 2
Results from measurements of the vapor pressure p

T (K)[a]	m (mg)[b]	$V(N_2)$ (dm^3)[c]	p (mbar)[d]	T (K)[a]	m (mg)[b]	$V(N_2)$ (dm^3)[c]	p (mbar)[d]
1-Nitropentane, $\Delta_{\mathrm{vap}}H^0=(50.30\pm0.21)$ kJ mol^{-1}							
278.5	4.70	2.470	0.4328	303.3	10.7	0.888	2.582
283.5	5.31	1.810	0.6506	308.4	10.5	0.619	3.622
288.4	6.26	1.510	0.9063	313.5	10.2	0.436	4.965
293.3	7.74	1.270	1.319	318.6	11.1	0.352	6.670
298.3	8.15	0.937	1.869				
Nitrocyclohexane, $\Delta_{\mathrm{vap}}H^0=(54.74\pm0.58)$ kJ mol^{-1}							
278.5	1.21	2.580	0.09515	303.3	3.19	0.928	0.6656
283.5	1.42	1.890	0.1493	308.4	3.13	0.647	0.9322
288.4	1.63	1.580	0.2032	313.5	3.23	0.456	1.363
293.3	2.23	1.320	0.3292	318.6	3.57	0.368	1.865
298.3	2.34	0.979	0.4646				
2,4,4-Trimethyl-2-nitropentane, $\Delta_{\mathrm{vap}}H^0=(54.18\pm0.79)$ kJ mol^{-1}							
288.5	2.45	1.220	0.3205	308.3	2.47	0.263	1.473
293.6	2.21	0.709	0.4930	313.5	2.61	0.198	2.058
298.3	2.16	0.461	0.7359	318.3	2.34	0.132	2.770
303.4	2.18	0.331	1.034	323.7	2.39	0.099	3.774
3-Nitro-3-(*p*-nitrophenyl)-pentane, $\Delta_{\mathrm{vap}}H^0=(87.99\pm0.75)$ kJ mol^{-1}							
321.4	0.265	58.67	0.0004705	343.5	1.02	26.45	0.004017
328.4	0.530	54.85	0.001005	348.3	0.795	13.31	0.006210
333.2	0.643	43.47	0.001540	353.2	1.10	12.73	0.008963
338.3	0.908	38.03	0.002483	358.1	2.04	14.75	0.01440
1,4-Dinitrobenzene, $\Delta_{\mathrm{sub}}H^0=(91.88\pm0.65)$ kJ mol^{-1}							
323.3	1.96	144.6	0.001995	338.2	2.44	39.69	0.009065
328.2	2.22	97.95	0.003340	343.3	4.85	46.59	0.01532
328.2	2.22	97.95	0.003340	348.3	8.77	54.91	0.02350
333.3	2.24	57.90	0.005701	353.3	10.1	41.26	0.03588
1,2-Dinitrobenzene, $\Delta_{\mathrm{sub}}H^0=(93.08\pm0.92)$ kJ mol^{-1}							
323.3	2.81	138.1	0.002995	343.3	6.88	43.83	0.02311
328.2	3.12	92.16	0.004983	348.3	1.29	51.67	0.03673
333.3	3.26	54.47	0.008797	353.3	1.47	38.64	0.05592
338.2	3.66	37.34	0.01444				
2-Amino-nitrobenzene, $\Delta_{\mathrm{sub}}H^0=(87.17\pm0.65)$ kJ mol^{-1}							
313.5	2.60	65.90	0.007124	333.3	9.77	33.36	0.05256
318.2	6.25	91.99	0.01225	338.4	19.0	40.35	0.08442
323.2	5.14	46.08	0.02007	342.3	9.25	13.46	0.1233
328.4	7.81	42.73	0.03282				

[a] Temperature of saturation, N_2 gas stream 0.26–0.52 cm^3 s^{-1}.

[b] Mass of transferred sample condensed at T=243 K.

[c] Volume of nitrogen used to transfer mass of sample m.

[d] Vapour pressure at T of experiment; corrections were made for residual vapour pressure at T=243 K.

Table 3
Results from typical combustion experiments at 298.15 K [a], where: nitrocyclohexane B, 2,4,4-trimethyl-2-nitropentane C and 3-nitro-3-(*p*-nitrophenyl)-pentane D

	B	C	D
m (substance) (g) [b]	0.566076	0.449956	0.409171
$m'_{(\mathrm{cotton})}$ (g) [b]	0.001049	0.000990	0.001051
$m''_{(\mathrm{polyethene})}$ (g)	0.278897	0.271219	0.046614 [e]
ΔT_c (K) [c]	1.16548	1.09506	0.50623
$\varepsilon_{\mathrm{calor}}(-\Delta T_c)$ (J)	−29268.12	−27499.83	−12712.85
$\varepsilon_{\mathrm{cont}}(-\Delta T_c)$ (J)	−16.40	−14.86	−6.58
ΔE_{corr} (J) [d]	12.12	9.60	7.05
$-m'\Delta_c u'$ (J)	17.77	16.77	17.80
$-m''\Delta_c u''$ (J)	12929.95	12573.99	2144.43
ΔE_{dec} (J)	36.72	29.85	26.87
$\Delta_c u$ (substance) (J g^{-1})	−28770.9	−33076.6	−25715.0

[a] For the definition of the symbols see Ref. [8], macrocalorimeter: T_h=298.15 K; V_{bomb}=0.2664 l; p^i_{gas}=3.04 MPa; m^i_{water}=0.78 g; $E_{\mathrm{ignition.}}$=1.5 J; m_{platin}=12.18 g.
[b] Corrected masses were taken into account.
[c] $\Delta T_c=T^f-T^i+\Delta T_{\mathrm{corr.}}$, $\varepsilon_{\mathrm{calor}}=(25112.6\pm1.9)$ J K^{-1}; $\varepsilon_{\mathrm{cont}}(-\Delta T_c)=\varepsilon^i_{\mathrm{cont}}(T^i-298\ \mathrm{K})+\varepsilon^f_{\mathrm{cont}}(298\ \mathrm{K}-T^f+\Delta T_{\mathrm{corr.}})$.
[d] $\Delta E_{\mathrm{corr.}}$ is the sum of items 81–85, 87–90, 93 and 94 in Ref. [8].
[e] Combustion with oil.

values of $\Delta_c u^0$, together with the mean and its standard deviation, are given in Table 4. To derive $\Delta_f H^0$ from $\Delta_c H^0$ the following molar enthalpies of formation were used [9](b): for H_2O(l): (-285.83 ± 0.04) kJ mol^{-1}, for CO_2(g): (-393.51 ± 0.13) kJ mol^{-1}. Table 5 lists the derived standard molar enthalpies of combustion and formation in the condensed and gaseous states. The given standard deviations of the mean include the uncertainties from calibration and the uncertainties from the combustion energies of the auxiliary materials.

Table 4
Values of massic energies of combustion $\Delta_c u^0$ at T=298.15 K as the results of all combustion experiments for nitro compounds: nitrocyclohexane B, 2,4,4-trimethyl-2-nitropentane C, and 3-nitro-3-(*p*-nitrophenyl)-pentane D

B	C	D
$-\Delta_c u^0$ (J g^{-1})		
28765.6	33076.6	25715.0
28770.9	33081.8	25712.1
28767.4	33055.0	25717.0
28772.8	33074.3	25720.5
28775.0	33094.2	25706.5
Mean value		
28770.3	33076.4	25714.2
±1.7	±6.4	±2.4

The resulting enthalpies of sublimation $\Delta_{\mathrm{sub}}H^0$ or vaporization $\Delta_{\mathrm{vap}}H^0$ at 298.15 K are recorded in Table 5. Because of the temperature range of vapour pressure measurements was usually above 298.15 K the derived values of enthalpies of vaporization or sublimation had been corrected to this reference temperature. The values of corrections were estimated using the 'Sidgwick correction':

$$\Delta_{\mathrm{vap}}H^0(T_{\mathrm{average}}) - \Delta_{\mathrm{vap}}H^0(298.15\ \mathrm{K}) = -0.06(T_{\mathrm{average}} - 298.15),$$

following the recommendation of Chickos et al. [15]. The values of the estimated corrections are given in Table 6. With these corrections and the measured values of $\Delta_{\mathrm{vap}}H^0(T)$ and $\Delta_{\mathrm{sub}}H^0(T)$ from Table 2, the standard molar enthalpies of vaporization or sublimation at T=298.15 K were calculated (Table 5). The value of the enthalpy of sublimation $\Delta_{\mathrm{sub}}H^0$= (110.77±0.78) kJ mol^{-1} of compound D was calculated as the sum of $\Delta_{\mathrm{vap}}H^0$= (90.48±0.75) kJ mol^{-1} (Table 6) and the enthalpy of fusion $\Delta_{\mathrm{fus}}H^0$= (20.29±0.21) kJ mol^{-1} measured by DSC.

3.1. Nitropentane

Value of the enthalpy of formation $\Delta_f H^0$(l)=(−215.4±1.5) kJ mol^{-1} of 1-nitropentane,

Table 5
Experimental results for nitro compounds A–G at T=298.15 K, where A=1-nitropentane, B=nitrocyclohexane, C=2,4,4-trimethyl-2-nitropentane, D=3-nitro-3-(p-nitrophenyl)-pentane, E=1,4-dinitrobenzene, F=1,2-dinitrobenzene, and G=2-amino-nitrobenzene

	State	Δ_cH^0 [a] (kJ mol^{-1})	Δ_fH^0 (l or cr) (kJ mol^{-1})	$\Delta_{vap}H^0$ or $\Delta_{sub}H^0$ [b] (kJ mol^{-1})	Δ_fH^0(g) (kJ mol^{-1})
A	l	—	−215.4±1.5 [c]	50.30±0.21	−165.1±1.5
B	l	−3719.08±0.38	−214.04±0.38	54.74±0.58	−159.30±0.69
C	l	−5273.6±1.1	−304.1±1.1	54.65±0.79	−249.5±1.4
D	cr	−6127.53±0.74	−201.88±0.74	110.77±0.78 [d]	−91.1±1.1
E	cr	—	−38.7±0.5 [e]	94.29±0.65	55.59±0.82
F	cr	—	−1.8±0.7 [e]	95.49±0.92	93.7±1.2
G	cr	—	−26.1±0.5 [f]	88.95±0.65	62.85±0.82

[a] Calculated from the massic enthalpies of combustion in Table 4.

[b] From the measurements of vapour pressure at different temperatures from Table 2 using the Clausius–Clapeyron equation.

[c] The result was taken from [12].

[d] The enthalpy of sublimation $\Delta_{sub}H^0$ was calculated as the sum of $\Delta_{vap}H^0 + \Delta_{fus}H^0$ (see text).

[e] The result was taken from [13].

[f] The result was taken from [14].

measured by the combustion calorimetry, has already been reported in the literature [12]. The measured value in this work $\Delta_{vap}H^0$=(50.30±0.21) kJ mol^{-1} allowed to derive Δ_fH^0(g)=(−165.1±1.5) kJ mol^{-1} for this compound for further interpretation in Table 8.

3.2. Compounds B, C, and D

No thermochemical properties were found for these compounds in the literature through 1997.

3.3. 4-Dinitrobenzene

Value of the enthalpy of formation for 1,4-dinitrobenzene Δ_fH^0(cr)=(−38.7±0.5) kJ mol^{-1} has been reported in the literature [13]. The values of enthalpies of sublimation from earlier works are given in Table 7. They are in agreement with our result within the bounds of the uncertainties.

3.4. 2-Dinitrobenzene

Lebedeva et al. [13] reported the enthalpy of formation of 1,2-di-nitrobenzene Δ_fH^0(cr)=(−1.8±0.7) kJ mol^{-1} using combustion calorimetry. The present derived value of the enthalpy of sublimation of F $\Delta_{fus}H^0$=(95.49±0.92) kJ mol^{-1} is essentially different from earlier results (see Table 7) and this discrepancy is not acceptable within the bounds of the experimental uncertainties.

3.5. 2-Amino-nitrobenzene

The enthalpy of formation of 2-amino-nitrobenzene have already been measured by Medard and Thomas

Table 6
Observed vaporization or sublimation enthalpies of nitro compounds corrected to T=298.15 K

	State	$T_{average}$ (K)	$\Delta_{vap}H^0$(obs.) (kJ mol^{-1})	δ (kJ mol^{-1})	$\Delta_{vap}H^0$(298.15 K) (kJ mol^{-1})
1-Nitropentane	l	298.5	50.30±0.21	0.00	50.30±0.21
Nitrocyclohexane	l	298.5	54.74±0.58	0.00	54.74±0.58
2,4,4-Trimethyl-2-nitropentane	l	306.1	54.18±0.79	+0.47	54.65±0.79
3-Nitro-3-(p-nitrophenyl)-pentane	cr	339.7	87.99±0.75	+2.49	90.48±0.75
1,4-Dinitrobenzene	cr	338.3	91.88±0.65 [a]	+2.41	94.29±0.65 [a]
1,2-Dinitrobenzene	cr	338.3	93.08±0.92 [a]	+2.41	95.49±0.92 [a]
2-Amino-nitrobenzene	cr	327.9	87.17±0.65 [a]	+1.78	88.95±0.65 [a]

[a] Enthalpy of sublimation $\Delta_{sub}H^0$.

Table 7
Comparison with earlier values of the enthalpy of sublimation (in kJ mol^{-1})

	$\Delta_{sub}H^0$ (298.15 K)	Reference
1,4-Di-nitrobenzene	91.8±1.7 [a]	[16]
	96.2±2.5	[18]
	94.29±0.65	This work
1,2-Di-nitrobenzene	88.7±1.7 [b]	[16]
	87.9±2.1	[18]
	95.49±0.92	This work
2-Amino-nitrobenzene	83.3±2.0 [c]	[16]
	87.4±4.2	[17]
	88.95±0.65	This work

[a] The observed value ($T_{average}$ 343 K) 89.1 kJ mol^{-1} was extrapolated (δ=2.7 kJ mol^{-1}) to 298.15 K.
[b] The observed value ($T_{average}$ 333 K) 86.6 kJ mol^{-1} was extrapolated (δ=2.1 kJ mol^{-1}) to 298.15 K.
[c] The observed value ($T_{average}$ 313 K) 82.4 kJ mol^{-1} was extrapolated (δ=0.9 kJ mol^{-1}) to 298.15 K.

[19] $\Delta_f H^0$(cr)=(−26.3±3.2) kJ mol^{-1} and later by Lebedeva et al. [14] $\Delta_f H^0$(cr)=(−26.1±0.5) kJ mol^{-1}. The agreement is excellent. The last and more precise value was selected for the estimation of the gaseous enthalpy of formation. The derived value of the enthalpy of sublimation of 2-amino-nitrobenzene of (88.95±0.65) kJ mol^{-1} is very close to the earlier result (Table 7) of Hoyer and Peperle [17] and essentially different from earlier result of Wolf and Weghofer [16].

3.6. *Calculation of strain-free increments of nitro compounds*

Strain-free group additivity increments for hydrocarbons are well defined [20,21]. Their advantage with respect to the classic Benson increments [1,2] is the possibility to determine strain enthalpies. The Benson type increments [1,5] for nitro compounds have not

Table 8
Calculation of the strain free increments of nitro compounds [a]

Compound	$\Delta_f H^0$ (g, 298.15 K)	Increment [b]	$\Delta_f H^0$(g) [c] (calc.)	Δ [d]
1	2	3	4	5
		$CH_3[NO_2]$		
Nitromethane	−74.3±0.5 [22]	−32.25	—	—
		$CH_2[NO_2, C]$		
Nitroethane	−102.3±0.6 [22]	−28.0	−102.1	−0.2
1-Nitropropane	−123.8±0.7 [22]	−28.0	−123.6	−0.2
1-Nitrobutane	−143.9±1.5 [22]	−26.7	−145.0	+1.1
1-Nitropentane (A)	−165.1±1.5 [e]	−26.4	−166.5	+1.4
		Mean: −27.8		
		$CH[NO_2, 2C]$		
2-Nitropropane	−139.0±0.9 [22]	−22.7	−140.8	+1.8
2-Nitrobutane	−163.6±1.6 [22]	−25.8	−162.2	−1.4
Nitrocyclohexane (B)	−159.30±0.69 [f]	−25.1	−158.6	−0.8
		Mean: −24.4		
		$C[NO_2, 3C]$		
2-Methyl-2-nitropropane	−177.1±3.3 [22]	−18.7	−178.0	+0.9
2,4,4-Trimethyl-2-nitropentane (C)	−249.5±1.4 [f]	−19.0	−250.1	+0.6
3-Nitro-3-(*p*-nitrophenyl)-pentane (D)	−91.1±1.1 [f]	−20.0	−90.7	−0.4
		Mean: −19.6	—	
		$C_B[NO_2, 2C_B]$		
Nitrobenzene	67.5±0.6 [22]	31.15	—	—

[a] All values in kJ mol^{-1}.
[b] Mean value was calculated under consideration uncertainty as statistical weight [24].
[c] Calculated as a sum of the strain free increments for alkanes (see Table 9) and nitro compounds (this Table). The strain enthalpy H_s: 5.4 kJ mol^{-1} (B), 34.7 kJ mol^{-1} (C), and 10.9 kJ mol^{-1} (D) was added to this calculated sum by molecules B, C and D.
[d] Calculated as the difference between column 2 and 4.
[e] Estimated from $\Delta_f H^0$ (l)=(−215.4±1.5) kJ mol^{-1} [12] and $\Delta_{vap}H^0$=(50.30±0.21) kJ mol^{-1} (this work, Table 6).
[f] From this work (Table 6).

Table 9

Strain free group increments [a] for calculation of the enthalpy of formation of alkanes, arenes, nitro- and amino-compounds at 298.15 K (in kJ mol^{-1})

ΔH_{alkane} [20]		ΔH_{arene} [21]		ΔH_{nitro}		ΔH_{amino} [26]	
$CH_3[C]$	−42.05			$CH_3[NO_2]$	−42.05		
$CH_2[2C]$	−21.46			$CH_2[NO_2, C]$	−27.8	$N[C_B, 2H]$	+16.6
$CH[3C]$	−9.04			$CH[NO_2, 2C]$	−24.4	$N[C_B, C, H]$	+65.4
$C[4C]$	−1.26	$C_BH[2C_B]$	+13.72	$C[NO_2, 3C]$	−19.6	$N[C_B, 2C]$	+115.2
		C_B $[C, 2C_B]$	+23.51	C_B $[NO_2, 2C_B]$	+31.15	C_B $[N]$	+2.1

[a] C_B represents the C atom in a benzene ring. Group additivity value of $NO_2[C]=-32.25$ kJ mol^{-1} (see text).

yet been deliberately adjusted to the strain-free hydrocarbon increments [20], but new results from this work together with the thermochemical data available from the literature [5,22,23] allowed us to calculate them. The set of standard molar enthalpies of formation $\Delta_fH^0(g)$ used for these calculations is presented in Table 8. We postulated the identity of groups CH_3 in alkanes and nitro compounds: $CH_3[C]\equiv CH_3[NO_2]=-42.05$ kJ mol^{-1} (Table 9). The increment $NO_2[C]=-32.25$ kJ mol^{-1} was calculated from the enthalpy of formation of nitromethane [22] and the part of this molecule $CH_3[NO_2]=-42.05$ kJ mol^{-1}. The complete incrementation of enthalpies of formation is listed in Table 8. The resulting mean values of the derived group increments are accomplished in Table 9.

In order to obtain strain-free increments the enthalpies of formation of strained molecules such as B, C, and D were corrected for strain. For these three compounds the strain enthalpies were estimated from the strain of the analogously branched hydrocarbons [22]: cyclohexane ($\Delta_fH^0(g)=-123.4$ kJ mol^{-1}) for B, 2,2,4,4-tetra-methylpentane ($\Delta_fH^0(g)=-241.6$ kJ mol^{-1}) for C, and tert-butylbenzene ($\Delta_fH^0(g)=-24.42$ kJ mol^{-1} [25]) for D. Using the sum of the appropriate hydrocarbon increments from Table 9 the following reference values of strain H_s: 5.4 kJ mol^{-1} (B), 34.7 kJ mol^{-1} (C), and 10.9 kJ mol^{-1} (D) were calculated. These values were taken into account by the estimation of strain-free increments from compounds B, C, and D (Table 8). The summary of the new group additivity values is given in Table 9.

3.7. Calculation of non-nearest neighbour interactions of substituents on benzene ring

Interactions between atoms which were separated by at least two other atoms were called non-nearest neighbour interactions. The result of such interactions caused in general a strain of molecule. We define the strain of a molecule, as the difference between the experimental standard enthalpy of formation $\Delta_fH^0(g)$ and the calculated sum of the strain-free increments (Table 9). The intrinsic strain of the nitrobenzene and aniline have been taken into account by the use of the additive terms $C_B[NO_2, 2C_B]$ (see Table 9) and $C_B[N, 2C_B]$ (from [26]) for a nitro and amino group attached to the benzene ring. The application of these terms allowed to derive the effects of non-nearest neighbour interactions of nitro and amino substituents on the benzene ring directly.

Because of the opposite nature of the π interactions between the benzene ring and either the nitro or the amino substituent, resulting interactions of substituents could lead to stabilization or destabilization of a molecule. Using the group-additivity parameters given in Table 9 and the values of $\Delta_fH^0(g)$ of the nitrobenzenes E, F, and G (Table 5) derived in this work, the values of excess interactions $\Delta\Delta=(\Delta_fH^0(g)-\Sigma$ increments) of substituents have been estimated.

The estimated quantities of the pairwise interactions of the nitro substituents indicated the very weak destabilization ($\Delta\Delta=+2.9$ kJ mol^{-1}) in *para* position of substituents. The *ortho* interaction of the two nitro groups led to the considerable destabilization ($\Delta\Delta=+41.0$ kJ mol^{-1}), which may be attributed to steric repulsions of the bulky substituents. One reason is that the *ortho* steric interaction is so great that the strain is partly relieved by rotation of a nitro group from planarity with the ring, thereby losing conjugation and raising the energy of the π system [23].

The resulting stabilization ($\Delta\Delta=-9.6$ kJ mol^{-1}) was detected by the *ortho* location of the nitro and amino substituents on the benzene ring. Interestingly, the *para* isomer (4-amino-nitrobenzene $\Delta_f H^0(g)$= (58.8±1.5) kJ mol^{-1} [22]) is of comparable stability ($\Delta\Delta = -13.7$ kJ mol^{-1}) to its *ortho* isomer.

4. Conclusions

A new ideal-gas enthalpies of formation of nitro compounds determined in this work allowed to estimate the group-additivity parameters for aliphatic nitro compounds and the correction terms for substituted nitrobenzenes which are necessary for the application of the Benson group-contribution correlation to get $\Delta_f H^0(g)$.

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