Journal of Thermal Analysis and Calorimetry, Vol. 60 (2000) 437–451

IMPROVED GROUP-ADDITIVITY VALUES FOR THE ESTIMATION OF THE STANDARD ENTHALPIES OF FORMATION OF IMINES AND CARBOXYLIC ACIDS DERIVATIVES

S. P. Verevkin[*]

Department of Physical Chemistry, University of Rostock, Hermannstr. 14, D-18051 Rostock
Germany

(Received August 26, 1999)

Abstract

This work has been undertaken for the evaluation and revision of group additivity values necessary for predicting gaseous standard enthalpies of formation of nitrogen and oxygen containing compounds by means of Benson's group additivity methodology. The current database of experimental data for enthalpies of formation, enthalpies of vaporization and enthalpies of sublimation was used to derive the values of the strain-free increments for imines, amides, oxo-amides, and carboxylic acids anhydrides. The group-additivity parameters and strain corrections useful in the application of the Benson correlation are presented in tabular form, together with a description of their evaluation and comments on their reliability.

Keywords: amides, carboxylic acid anhydrides, group-additivity correlation, imides, N-oxo-amides, standard enthalpy of formation

Introduction

Thermodynamic properties of organic compounds in general can be estimated using quantitative structure-property relationships where the property of interest is a function of molecular descriptors that can be derived in either non-empirical or empirical ways. Examples of the empirical techniques are the well-known group-additivity procedures [1–3], where the property is estimated as the sum of contributions from the individual structural increments that compose the compound of interest. Ab initio calculations are still not appropriate for the relatively large species, because of the need for extensive computing resource and time [4].

Compounds containing the imine functionality (C=N) are of increasing interest in agricultural and pharmaceutical research [5], and so there is a need for thermodynamic information. Reliable thermochemical information for imines is sparse [6–8].

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[*] E-mail: sergey.verevkin@chemie.uni-rostock.de

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Our recent investigation of the eight (C=N)–containing compounds covered a broad range of structures of imines [9]. Results from this work together with the same data available for the literature [6–8] were taken as a basis for the evaluation of group additivity value of imines, thus expanding the applicability of Benson's methodology into this class of compounds.

Thermochemical data for many carboxylic acids derivatives have been included in several comparatively recent compilations [3, 10–12]. Recently amides have been extensively studied, both experimentally [13–26] and theoretically [27]. Although, the group-additivity values for amides were already derived in [1, 3], the additive parameters for amides and oxo-substituted amides were not the subject of revaluation during the last ten years. Because of the paucity of experimental data at that time, the numbers of additive parameters for amides [1, 3] were derived from one or two compounds and some parameters were not available. The thermochemical data available at that time were not consistent, as they should be if they are to be used for an accurate prediction. Thus, these group-additivity values of nitrogen containing compounds have to be re-calculated and extended, using the contemporary experimental results [13–26]. This paper extends our previous studies on the systematic evaluation of the group-additivity values for amino [29–35], oxygen [36–40], and halogen [41] containing organic compounds. We would like to report here, the empirical group-additivity increments that have been improved, to estimate the standard enthalpies of formation of imides, amides, oxo-amides and carboxylic acid anhydrides.

Imines

Calculation of strain-free increments of imines

Strain-free group additivity increments for hydrocarbons are well defined [42–43]. Their advantage with respect to the classic Benson increments [1–2] is the possibility to determine strain enthalpies. The Benson type increments [1–2] for imines have not yet been deliberately adjusted to the strain-free hydrocarbon increments [42], but our recent results [9] together with the thermochemical data available from the literature [6–8] allowed for this evaluation. The set of standard molar enthalpies of formation $\Delta_f H_m^0$ (*g*) used for this procedure are presented in Table 1. We postulated the identity of groups CH_3 in alkanes and imines: CH_3 [C]≡CH_3 [N_I]= –42.05 kJ mol^{-1} (Table 1). We also postulated the identity of groups C_d in alkenes and imines: C_d [C_d]$_i$≡C_d [N_I] (Table 1). For the estimation of the new increments N_IH [C_d], N_I [C_d, C] and N_I [C_d, C_B], the increments recorded in Table 2 were used. The earlier derived [34] increments of amines: CH_3[N], CH_2 [N, C], CH [N, 2C] and C_B [N] (Table 2), were taken to be identical for imines. To derive the increment N_IH [C_d]=32.1 kJ mol^{-1} we used only the enthalpy of formation of benzophenone-imine. Increment N_I [C_d, C]= 77.9 kJ mol^{-1} was calculated as the mean value from the experimental results of compounds: N-methyl-benzaldehyde-imine (77.6 kJ mol^{-1}), N-benzyl-benzaldehyde-imine (80.6 kJ mol^{-1}), N-cyclohexyl-(2,4,6-trimethyl)-benzaldehyde-imine (79.5 kJ mol^{-1}), N-tert-butyl-(4-nitro)-benzalde- hyde-imine (69.9 kJ mol^{-1}), N-cycl-

Table 1 Calculation of the strain-free increments of imines (in kJ mol^{-1})[a]

Increment	Compound	Formula	$\Delta_f H^o_m$ (g)/ 298.15 K[b] exp.	$\Delta_f H^o_m$ (g) calc.	Δ	$\Delta_f H^o_m$ (g) calc. PM3 [52]	$\Delta_f H^o_m$ (g) calc. AM1 [52]
N_IH [C_d]	Benzophenone-imine	$C_{13}H_{11}N$	248.4±2.1 [9]	248.1	–	291.2	295.9
N_I [C_d, C]	N-methyl-benzaldehyde-imine	C_8H_9N	157.1±1.4 [9]	157.3	–0.2	162.4	178.5
	N-benzyl-benzaldehyde-imine	$C_{14}H_{13}N$	268.8±2.3 [9]	264.5	4.3	283.3	298.1
	N-benzyl-pivalophenone-imine	$C_{18}H_{21}N$	(156.4±4.2) [9]	148.9	(7.5)	191.5	238.2
	N-cyclohexyl-(2,4,6-tri-methyl)-benzaldehyde-imine	$C_{13}H_{22}N$	–23.2±2.8 [9]	–24.8	1.6	–19.5	–3.3
	N-tert-butyl-4-nitro-benzaldehyde-imine	$C_{11}H_{14}N_2O_2$	49.4±3.6 [8]	57.4	–8.0	–	–
	N-(2-methylpropylidene)-butylamine	$C_8H_{17}N$	–91.2±5.4 [47]	–91.1	0.1	–	–
	dibenzylidene-1,2-ethande-diamine	$C_{16}H_{16}N_2$	355.1±8.6 [10, 48]	344.8	10.3	–	–
N_I [C_d, C_B]	N-phenyl-benzaldehyde-imine	$C_{13}H_{11}N$	279.7±2.5 [9]	278.4	1.3	289.7	308.5
	N-phenyl-4-nitro-benzaldehyde-imine	$C_{13}H_{10}N_2O_2$	263.5±2.3 [9]	263.8	–0.3	254.1	325.6
	N-phenyl-benzophenone-imine	$C_{19}H_{15}N$	372.2±3.4 [9]	373.2	–1.0	404.0	436.1

[a] Values in brackets were not taken into account by estimation of strain-free increments

[b] The uncertainties of imines reported in the reference [9] have been recalculated in this work, taking into account additionally the uncertainties of the combustion reaction products H_2O and CO_2 [46]

Table 2 Strain-free increments for estimation of $\Delta_f H_m^o$ (*g*) at *T*=298.15 K of hydrocarbons, nitrogen, and oxygen containing compounds

Group	Value/kJ mol^{-1}	Group	Value/kJ mol^{-1}	Group	Value/kJ mol^{-1}
CH_3[C]	–42.05 [42]	CH_3[N]	–42.05	CH_3[CO]	–42.05
CH_2[2C]	–21.46 [42]	CH_2[N, C]	–26.9 [34]	CH_2[CO, C]	–21.8 [37]
CH[3C]	–9.04 [42]	CH[N, 2C]	–20.0 [34]	CH[CO, 2C]	–10.0 [37]
C[4C]	–1.26 [42]	C[N, 3C]	–16.1 [34]	C[CO, 3C]	2.6 [37]
				CO[2C]	–130.54 [37]
$CH_2[C_d$, C]	–21.46[b]	NH_2[C]	19.4 [34]	NH_2[CO]	–62.5±0.9
$CH[C_d$, 2C]	–9.04[b]	NH[2C]	64.1 [34]	NH[CO, C]	–20.2±1.4
$C[C_d$, 3C]	–1.26[b]	N[3C]	103.2 [34]	N[CO, 2C]	27.8±1.1
				HCO[C, N]	–131.1±1.7
				CO[C, N]	–130.54
$C_BH[2C_B]$	13.72 [43]				
$C_B[C, 2C_B]$	23.51 [43]	$C_B[N, 2C_B]$	2.1 [34]	$C_B[CO, 2C_B]$	18.0 [37]
$C_B[C_d, 2C_B]$	24.3 [2]	$NH_2[C_B]$	16.6 [34]		
$C_dH_2[C_d]$	26.4 [2]	$NH[C_B, C]$	65.4 [34]	$NH[CO, C_B]$	–18.5±1.9
$C_dH[C_d, C]$	36.0 [2]	$N[C_B, 2C]$	115.2 [34]	$N[CO, C_B, C]$	26.8±3.3
$C_d[C_d, 2C]$	42.7 [2]				
$C_dH[C_d, C_B]$	28.4 [2]	$N_IH[C_d]$	32.1±2.1		
$C_d[C_B, C, C_d]$	40.3 [64]	$N_I[C_d, C]$	77.9	NH[2CO]	–79.5
$C_d[2C_B, C_d]$	30.4 [65]	$N_I[C_d, C_B]$	86.3±0.7	N[2CO, C]	–17.4
		$C_B[NO_2, 2C_B]$	31.5 [30]		
		NO_2[C]	–32.3 [30]	O[2CO]	–231.0

[a] C_d represents a double-bonded C atom, C_B the C atom in a benzene ring, N_I represents the N atom in an imine

[b] Strain free increments were adopted to be equal of those in alkanes [42, 43, 65]

ohexyl-(2,4,6-trimethyl)-benzaldehyde-imine), N-(2-methylpropylidene)-butylamine (77.8 kJ mol^{-1}), and dibenzylidene-1,2-ethane-diamine (83.1 kJ mol^{-1}). The mean value of increment N_I [C_d, C] was calculated taking into consideration the uncertainty as a statistical weighting factor [49]. The molecule of N-benzyl-pivalophenone-imine apparently possesses an inherent strain of 7.5 kJ mol^{-1} (Table 1) due to repulsion's of phenyl and tert-butyl substituents attached to the sp^2 hibridised carbon atom, therefore its enthalpy of formation was not included in the calculation of strain-free increments. The mean value of the increment N_I [C_d, C_B]= 86.3 kJ mol^{-1} was calculated from the enthalpies of formation of compounds N-phenyl-benzaldehyde-imine (87.6), N-phenyl-4-nitro-benzaldehyde-imine (86.0), N-phenyl-benzophenone-imine (85.3). Summary of the increments used and derived is presented in Table 2.

Prediction of the enthalpies of formation of simple imines

The enthalpies of formation of simple imines has been the subject of several experimental [6–8] and theoretical studies [5, 44]. For example, the reported enthalpies of formation of methanimine, $NH{=}CH_2$, range from 69 to 134.7 kJ mol^{-1} [44]. In the absence of reliable experimental data with which to compare, strain-free increments derived in this work can serve for the prediction of enthalpies of formation of these important species (Table 3). The new increments N_IH [C_d] and N_I [C_d, C] from this work (Table 2) were used for the estimation of standard enthalpies of formation of some imines (Table 3). It gives the possibility of verifying these increments by calculation of $\Delta_f H^0_m$ (*g*) of methanimines and ethanimine, whose enthalpies of formation are recorded in the literature [5–7]. Predicted for methanimine $CH_2{=}NH$ the enthalpy of formation $\Delta_f H^0_m$ (*g*)=58.5 kJ mol^{-1} is in good agreement with the experimental results of Peerboom *et al.* [6] 69.8±8 kJ mol^{-1} and Holmes *et al.* [7] 87.9±16.7 kJ mol^{-1} when taking into account the experimental uncertainties of these measurements. A

Table 3 Comparison of calculated enthalpies of formation $\Delta_f H^o_m$ (*g*) at 298.15 K of imines to literature values (in kJ mol^{-1})

Compound	$\Delta_f H^o_m$ (*g*) exp.	$\Delta_f H^o_m$ (*g*) calc. G2	$\Delta_f H^o_m$ (*g*)^a predicted	Δ^b
$NH{=}CH_2$	69±8 [6]	86.0 [45]	58.5	27.5
$NH{=}CH{-}CH_3$	24±8 [6]	42.6 [5]	26.1	16.5
$NH{=}CH{-}CH_2{-}CH_3$		24.2 [5]	4.6	19.6
$NH{=}C(CH_3)_2$		0.4 [5]	–9.3	9.7
$CH_3{-}N{=}CH_2$	44±8 [6]	79.2 [5]	62.3	16.9
$CH_3{-}N{=}CH{-}CH_3$		35.6 [5]	29.8	5.8
$CH_3{-}CH_2{-}N{=}CH_2$		52.2 [5]	35.4	16.9

[a] Predicted using strain-free increments from Table 2

[b] Difference between G2 estimates and values predicted from strain-free increments from this work

very good agreement of the calculated value of $\Delta_f H_m^0$ (*g*)=26.1 kJ mol^{-1} with the experimental 24±8 kJ mol^{-1} was observed for ethanimine CH_3–CH=NH. The estimated value of $\Delta_f H_m^0$ (*g*)=62.3 kJ mol^{-1} for N-methyl-methanimine CH_2=N–CH_3 was, however, in poor agreement with the experimental result 44±8 kJ mol^{-1} of Peerboom *et al.* [6]. No definitive explanation for this can be offered at this time. The results from ab initio G2 calculations [5, 44–45] of enthalpies of formation of simple imines are overestimated in comparison with our predicted values which range from 5.8 to 27.5 kJ mol^{-1}, refer to the Table 3. However, such discrepancies could not be justified to within an accuracy of ±4–8 kJ mol^{-1}, claimed for the G2-method [5]. The available enthalpies of formation of the imines (Table 1) were also calculated by the semiempirical AM1 and PM3 methods. The data in Table 1 show a relatively smaller deviation from the experimental results for the PM3 values (4–35 kJ mol^{-1} deviation) than for the AM1 data (10–84 kJ mol^{-1} deviation). Both approximations still fail to provide the reasonable accuracy by estimation of the enthalpy of formation of imines. At the same time, the reasonable accuracy $\Delta = \Delta_f H_m^0$ (*g*, exp.)–$\Delta_f H_m^0$ (*g*, calc.) demonstrates the success (within the boundaries of experimental uncertainties of about ±2–10 kJ mol^{-1}) by the application of our new increments for the calculation of enthalpies of formation of the different imines (Table 1).

Amides

Evaluation of strain-free increments of amides

Experimental investigation of the thermochemistry of amides has been a popular endeavour recently [3, 13–26]. The body of thermochemical data for amides is considerable (Table 4). Vapor pressures and enthalpies of vaporization, however, are scarce, especially for the branched members of the series. In order to obtain $\Delta_f H_m^0$ (*g*) for those compounds from known data for $\Delta_f H_m^0$ (*liq.* or *cr.*) and to involve experimental data for the interpretation in gaseous state, the standard enthalpies of vaporization $\Delta_l^g H_m^0$ or sublimation $\Delta_{cr}^g H_m^0$ have to be assessed by any available methods. There is a plethora of sophisticated or simple procedures that have been developed for the prediction of the enthalpies of vaporization [68–69]. Taking into account that interpolation within the homological row always provides very reliable results [69], a method based on the determination of a partial contributions into $\Delta_l^g H_m^0$ due to extending of the alkane chain of homologues was employed. For instance: the difference between vaporization enthalpy of N-ethyl-N-butylamine and of N-methyl-N-butylamine represents the contribution of a CH_2-group in amines. Thus, having the experimental enthalpy of vaporization of N,N-di-methyl-propanamide, the unknown enthalpy of vaporization of N-methyl-N-ethyl-propanamide could be assessed with help of the defined contribution for CH_2-group. The enthalpy of vaporization results calculated in this way are recorded in Table 4. In some cases the experimental values of enthalpies of sublimation of amides were available from the compilation of Stephenson and Malanowski [53]. The deviations of the average temperatures from 298.15 K are large hence the experimental enthalpies of subli-

Table 4 Database for the calculation of the strain free increments of amides (in kJ mol^{-1})

Increment	Compound	Formula	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ (*g*)/298.15 K exp.[a]	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ (*g*) calc.	Δ
NH_2[CO]	Formamide	CH_3NO	–190.8[b]	–193.7	2.9
	Acetamide	C_2H_5NO	–238±0.9 [3]	–235.1	–3.2
	Propanamide	C_3H_7NO	–258.9±0.6 [3]	–256.9	–2.0
	Butanamide	C_4H_9NO	–279.1±0.9 [3]	–278.4	–0.7
	Pentanamide	$C_5H_{11}NO$	(–290.2±1.2) [3]	–299.8	9.6
	Hexanamide	$C_6H_{13}NO$	–324.2±1.8 [3]	–321.3	–2.9
	Octanamide	$C_8H_{17}NO$	–362.7±3.0 [3]	–364.2	1.5
	2-phenyl-acetamide	C_8H_9NO	–218.4[c]	–214.8	–3.6
	2-methyl-propanamide	C_4H_9NO	–282.6±0.9 [14]	–287.2	4.6
	2,2-di-methyl-propanamide	$C_5H_{11}NO$	–313.1±1.4 [14]	–316.7	3.6
	Benzamide	C_7H_7NO	–104.2[d]	–106.5	2.3
NH[CO, C]	N-methyl-formamide	C_2H_5NO	191.2±2.0 [26]	–193.3	2.1
	N-methyl-acetamide	C_3H_7NO	(–248.0±5.5) [54]	–234.5	–13.2
	N-methyl-propanamide	C_4H_9NO	–255.21±0.84[e]	–256.6	1.4
	N-butyl-acetamide	$C_6H_{13}NO$	–305.9±1.7 [3]	–304.5	–1.3
	N-butyl-pentanamide	$C_9H_{19}NO$	–371.5[f]	–369.3	2.2
NH[CO, Ph]	N-phenyl-acetamide	C_8H_9NO	–121.4[g]	–120.4	–1.0
	N-(2-methyl-phenyl)-acetamide	$C_9H_{11}NO$	(–144.7)[h]	–152.7	8.0
	N-(2,4-di-methyl-phenyl)-acetamide	$C_{10}H_{13}NO$	–183.9[i]	–184.9	1.0
N[CO, 2C]	N,N-di-methyl-formamide	C_3H_7NO	–192.4±1.6 [3]	–187.4	–5.0
	N,N-di-methyl-acetamide	C_4H_9NO	–228.1±1.8 [3]	–228.9	0.8
	N,N-di-ethyl-acetamide	$C_6H_{13}NO$	–281.3±3.2[j]	–282.7	1.4
	N,N-di-methyl-propanamide	$C_5H_{11}NO$	–250.2 [56]	–250.6	0.4
	N-methyl-N-ethyl-propanamide	$C_6H_{13}NO$	–275.6[k]	–277.5	1.9
	N,N-di-methyl-butanamide	$C_6H_{13}NO$	–270.9 [56]	–272.1	1.2
	N,N-di-methyl-pivaloamide	$C_7H_{15}NO$	(–286.1±2.1) [17]	–310.4	24.3
	N,N-di-methyl-nonanamide	$C_{11}H_{23}NO$	–374.0 [56]	–373.3[l]	–0.7
	N,N-di-methyl-benzamide	$C_9H_{11}NO$	(–86.0±2.2) [17]	–100.2	14.2
	N,N-4-tri-methyl-benzamide	$C_{10}H_{13}NO$	(–112.7±10.4) [21]	–132.5	19.8

Table 4 Continued

Increment	Compound	Formula	$\Delta_f H^\circ_m$ (*g*)/298.15 K exp.[a]	$\Delta_f H^\circ_m$ (*g*) calc.	Δ
N[CO, C, Ph]	N-methyl-N-phenyl-formamide	C_8H_9NO	–75.60 [20]	–75.6	
N[CO, 2Ph]	N,N-diphenyl-acetamide	$C_{14}H_{13}NO$	(81.8±7.1)[m]	–3.4	58.2

[a] Values of enthalpies of formation in brackets were not taken into account by calculation of increments. [b] Formamide: $\Delta_f H^\circ_m$ (*liq*)=–251.0 kJ mol^{-1} [50], $\Delta^g_l H^\circ_m$=60.15 kJ mol^{-1} [51]; [c] 2-Phenyl-acetamide: $\Delta_f H^\circ_m$ (*cr*)=–224.0±3.8 kJ mol^{-1} [13], $\Delta^g_{cr} H^\circ_m$=96.4 kJ mol^{-1} measured in interval (329–352 K) [53] was extrapolated to the reference temperature using Eq. (1): $\Delta^g_{cr} H^\circ_m$ (298.15 K)=97.8 kJ mol^{-1}. [d] Benzamide; $\Delta_f H^\circ_m$ (*cr*)=–202.14±0.60 kJ mol^{-1} [23], $\Delta^g_{cr} H^\circ_m$=96.9 kJ mol^{-1} measured in interval (325–342 K) [53] was extrapolated to the reference temperature using Eq. (1): $\Delta^g_{cr} H^\circ_m$ (298.15 K)=98.0 kJ mol^{-1}. [e] N-methyl-propanamide: $\Delta_f H^\circ_m$ (*liq*)=–320.1±0.8 kJ mol^{-1} [15], enthalpy of vaporization was $\Delta^g_l H^\circ_m$=64.89±0.25 kJ mol^{-1} [70]. [f] N-butyl-pentanamide: $\Delta_f H^\circ_m$ (*cr*)=–465.1±1.7 kJ mol^{-1} [3], $\Delta^g_{cr} H^\circ_m$=93.6 kJ mol^{-1} was calculated using Eq. (2). [g] N-phenyl-acetamide: $\Delta_f H^\circ_m$ (*cr*)=–209.5±1.5 kJ mol^{-1} [59], $\Delta^g_{cr} H^\circ_m$=87.2 kJ mol^{-1} measured in interval (317–336 K) [53] was extrapolated to the reference temperature using Eq. (1): $\Delta^g_{cr} H^\circ_m$ (298.15 K)=88.1 kJ mol^{-1}. [h] N-(2-methyl-phenyl)-acetamide $\Delta_f H^\circ_m$ (*cr*)=–242.4 ±0.8 kJ mol^{-1} [22], $\Delta^g_{cr} H^\circ_m$= 96.8 kJ mol^{-1} measured (315–340 K) [53] extrapolated to the reference temperature using Eq. (1): $\Delta^g_{cr} H^\circ_m$ (298.15 K)=97.7 kJ mol^{-1}. [i] N-(2,4-di-methyl)-acetamide: $\Delta_f H^\circ_m$ (*cr*)=–291.2±0.8 kJ mol^{-1} [22], $\Delta^g_{cr} H^\circ_m$=107.3 kJ mol^{-1} was calculated using enthalpy of sublimation of N-(2-methyl-phenyl)-acetamide; contribution into $\Delta^g_{cr} H^\circ_m$ (298.15 K) from methyl substituent was assessed as the difference of sublimation enthalpies of N-phenyl-acetamide and N-(2-methyl-phenyl)-acetamide.

[j] N,N-diethyl-acetamide: $\Delta_f H^\circ_m$ (*liq*)=–335.4±3.2 kJ mol^{-1} [16], enthalpy of vaporization $\Delta^g_l H^\circ_m$=54.11 ±0.20 kJ mol^{-1} [71].

[k] N-methyl-N-ethyl-propanamide: $\Delta_f H^\circ_m$ (*liq*)=–336.0±0.5 kJ mol^{-1} [3, 59], enthalpy of vaporization was assessed using $\Delta^g_l H^\circ_m$=55.89 kJ mol^{-1} [56] of N,N-dimethyl-propanamide and the difference between $\Delta^g_l H^\circ_m$=40.2 kJ mol^{-1} [51] of N-ethyl-N-butylamine and $\Delta^g_l H^\circ_m$=32.9 kJ mol^{-1} [81] of N-methyl-N-butylamine; result: $\Delta^g_l H^\circ_m$=52.9+7.3=60.2 kJ mol^{-1}. [l] Strain enthalpy of nonane H_s=6.1 kJ mol^{-1} [10] was taken into account by calculation of increment. [m] N,N-diphenyl-acetamide; $\Delta_f H^\circ_m$ (*cr*)=–42.9±7.1 kJ mol^{-1} [22], $\Delta^g_{cr} H^\circ_m$=122.7 kJ mol^{-1} measured (343–376 K) [53] was extrapolated to the reference temperature using Eq. (1): $\Delta^g_{cr} H^\circ_m$ (298.15 K)=124.7 kJ mol^{-1}

mation values (Table 4) had to be corrected to this reference temperature. The corrections were estimated with help of correlation:

$$\{\Delta^{g}_{cr}H^{0}_{m}(<T>)-\Delta^{g}_{cr}H^{0}_{m}(298.15\,\mathrm{K})\}/(\mathrm{kJ\,mol^{-1}})=-3.20\cdot10^{-2}\cdot\{(<T>/\mathrm{K})-298.15\} \quad (1)$$

following the recommendation of Chickos *et al.* [66]. With these corrections and the experimental observed values of $\Delta^{g}_{cr}H^{0}_{m}$ the standard molar enthalpies of formation of amides at T=298.15 K were calculated (Table 4).

Amides and their thermochemical properties considered for the evaluation of strain-free increments are listed in Table 4. The information concerning simple primary amides, $RCONH_2$ and N,N-dialkylamides $RCONR^1R^2$ is very representative. Unfortunately, N-alkyl-amides ($RCONHR^1$), N-phenyl-amides (RCONHPh), and N,N-diphenyl-amides ($RCONPh_2$) have not been investigated thoroughly, and this has thwarted the evaluation of reliable parameters for these species.

We put into the correlation the set of 22 experimental data for amides and handled them by polyfunctional least-square quadrate treatment. The average standard deviation through all involved compounds was 2.8 kJ mol^{-1}. In the calculation of standard deviation of the mean values of new increments the standard deviations for the known increments [2, 34, 37, 42] were not taken into account. The calculated values of strain-free increments for amides (Table 2) now provide more precise and reliable information, because the new current increments is a reflection of all the available experimental values. It is important to note, that increments NH[CO,C] and NH[CO, Ph] are indistinguishable within the experimental uncertainties, therefore, the possible conjugation between double bond of CO-group and phenyl ring is negligible. The same trend is observed by comparison of increments N[CO, 2C] and NH[CO, Ph, C].

A few compounds (Table 4) were excluded from the evaluation of increments: except for pentanamide, N-methyl-acetamide, N-methyl-propanamide, and N-(2-methyl-phenyl)-acetamide enthalpies of formation amides can be reasonably estimated by application of the strain-free increments derived in this work. It is quite unrealistic to expect any structural peculiarities of these compounds, leading to deviations from the additivity rules, therefore, the experimental values for these compounds should be the subject for a reinvestigation. Some other compounds: N,N-di-methyl-pivaloamide, N,N-di-methyl-benzamide, N,N,4-tri-methyl-benzamide, and N,N-diphenyl-acetamide (Fig. 1) were also excluded from the evaluation of increments due to their apparent conventional strains H_s, which were analysed in details by Abboud *et al.* [17] recently.

Estimation of strain enthalpies H_s of N,N-alkylated amides

Stabilisation or destabilisation is always relative and strain energy, resonance energy or conjugation could be derived only through comparison of the molecule in question with an appropriate reference (sum of increments) or a model compound. We define the strain of a molecule, as the difference between the experimental standard enthalpy of formation $\Delta_f H^{0}_{m}$ (*g*) and the calculated sum of the additive increments of strain

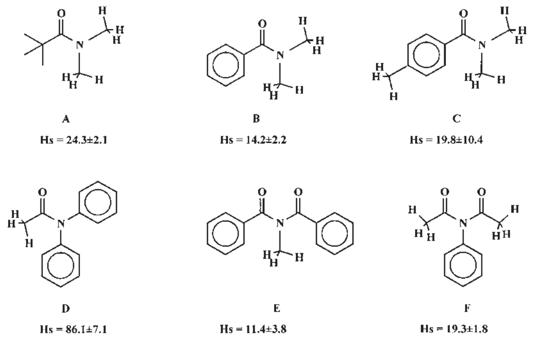

Fig. 1 Structures of strained amides: A – N,N-dimethyl-pivaloamide; B – N,N-di-methyl-benzamide; C – N,N,4-tri-methyl-benzamide; D – N,N-diphenyl-acetamide; E – N-benzoyl-N-methyl-benzamide, and F – N-acetyl-benzamide

free group increments [42] for the molecule. Using the group-additivity parameters from Table 2 and the experimental values of $\Delta_f H^0_m$ (*g*) from Table 4, the values of strain enthalpies H_S=($\Delta_f H^0_m$ (*g*)–Σ increments) of strained amides (Table 4) have been estimated. The resulting interactions are presented in graphic form in Fig. 1. These strain enthalpies (or correction terms) can be useful for the prediction of thermodynamic properties of unknown and new amides with similar structures.

Oxo-amides

Calculation of strain-free increments of oxo-amides

The set of thermochemical data for oxo-amides, available from the literature, is suprisingly scarce (Table 5). From the seven listed in Table 5, values for sublimation enthalpies for three of the compounds are unknown. However, methods of the prediction of the $\Delta^g_{cr} H^0_m$ are very rough [68]. In this work we have employed the recent method developed from the multilinear regression analysis (MLRA) of the $\Delta^g_{cr} H^0_m$ for the restricted classes of compounds [67]:

$$\Delta^g_{cr} H^0_m/\text{kJ mol}^{-1}=2.5+5.9C+19.0HBD+9.5HBA \quad (2)$$

where *C* is number of C-atoms in a molecule; *HBD* is parameter, which reflects potential for intermolecular H-bonding (number of H attached to heteroatoms); and *HBA* is parameter, which reflects the polar nature of functional group in a molecule (total number of heteroatoms). The general accuracy of this procedure was claimed to be better than 6.7 kJ mol^{-1} [67]. We tested this method by calculation of $\Delta^g_{cr} H^0_m$ of the relevant compounds with the known data (Table 6). The results from MLRA-method reproduced the experimental values for amides to within 1–3 kJ mol^{-1}. Thus, with help of this method, enthalpies of sublimation for N-(1-oxo-propyl)-propanamide, N-acetyl-N-phenyl-acetamide, and N-acetyl-benzamide were estimated. With these values and the experimental values of $\Delta_f H^0_m$ (*cr*), the gaseous standard molar enthalpies of formation of oxo-amides were obtained (Table 5) and were used in the evaluation of strain-free increments.

Table 5 Database for the calculation of the strain free increments of oxo-amides (in kJ mol^{-1})

Compound	Formula	$\Delta_f H^o_m$ (*g*)/298.15 K exp.	$\Delta_f H^o_m$ (*g*) calc.	Δ
N-acetyl-acetamide	$C_4H_7NO_2$	–427.6[b]	–424.7	–2.9
N-(1-oxo-propyl)-propanamide	$C_6H_{11}NO_2$	–465.3[c]	–468.2	+2.9
N-acetyl-N-butyl-acetamide	$C_8H_{15}NO_2$	–474.5±1.8 [3]	–474.5	–
N-acetyl-benzamide	$C_9H_9NO_2$	(–270.1)[d]	–296.5	26.4
N-acetyl-N-phenyl-acetamide	$C_{10}H_{11}NO_2$	(–272.6±1.8 [3]	–291.9	19.3
N-benzoyl-benzamide	$C_{14}H_{11}NO_2$	(–112.2)[e]	–168.4	56.2
N-benzoyl-N-methyl-benzamide	$C_{15}H_{13}NO_2$	(–119.5±3.8) [25]	–130.9	11.4

[a] Values of enthalpies of formation in brackets were not taken into account by calculation of increments. [b] N-acetyl-acetamide: $\Delta_f H^o_m$ (*cr*)=–500.8 kJ mol^{-1} [60] and $\Delta^g_{cr} H^o_m$=73.2±0.8 kJ mol^{-1} [55]. [c] N-(1-oxo-propyl)-propanamide: $\Delta_f H^o_m$ (*cr*)=–550.9 kJ mol^{-1} [61] and $\Delta^g_{cr} H^o_m$=85.6 kJ mol^{-1} calculated using Eq. (2). [d] N-acetyl-benzamide: $\Delta_f H^o_m$ (*cr*)=–373.2 kJ mol^{-1} [61] and $\Delta^g_{cr} H^o_m$=103.1 kJ mol^{-1} calculated using Eq. (2). [e] N-benzoyl-benzamide: $\Delta_f H^o_m$ (*cr*)=–244.8 kJ mol^{-1} [61] and $\Delta^g_{cr} H^o_m$=132.6 kJ mol^{-1} calculated using Eq. (2)

Table 6 Summary of auxiliary thermochemical properties using for the calculation of enthalpy of sublimation of oxo-amides using MLRA method [67] (in kJ mol^{-1})

	$\Delta^g_{cr} H^o_m$/exp.	$\Delta^g_{cr} H^o_m$ /calc.
N-acetyl-acetamide	73.2±0.8 [55]	73.6
N-acetyl-N-phenyl-acetamide	90.0±0.8 [3]	90.0
N-benzoyl-N-methyl-benzamide	120.1±0.4 [25]	119.5
2-methyl-propanamide	86.0±0.2 [14]	83.1
Benzamide	98.0 [53]	100.8
N-phenyl-acetamide	88.1 [53]	87.7

Increment NH [2CO]= –79.5 kJ mol^{-1} was calculated as the mean value from the experimental results of compounds: N-acetyl-acetamide (–82.4 kJ mol^{-1}) and N-(1-oxo-propyl)-propanamide (–76.6 kJ mol^{-1}). Unfortunately, the increments NH [2CO] derived from N-acetyl-N-phenyl-acetamide and N-acetyl-benzamide are about 20 kJ mol^{-1} different from mean value –79.5 kJ mol^{-1}, which may be due to the fact that the results for latter compounds were taken from a very old publication [61]. Increment N [2CO, C]=–17.4 kJ mol^{-1} was calculated only from N-acetyl-N-butyl-acetamide. N-benzoyl-benzamide could not be used for the evaluation of the increment N [2CO, C], because this compound is strained in a similar way as other similarly shaped amides (Fig. 1). The same reason has thwarted the use of the data for N-acetyl-benzamide for the evaluation of the increment N [2CO, C]. The conventional strain enthalpies of the latter compounds reported in Table 5 can be useful as correction terms for the prediction of thermodynamic properties of unknown and new oxoamides with similar structures.

Acid anhydrides

Calculation of strain-free increments of acid anhydrides

Experimental data for acid anhydrides are listed in Table 7. Similarly to the procedure described for oxo-amides we completed the set of useful $\Delta_f H_m^0$ (*g*) with the prediction of the missing enthalpies of sublimation by MLRA-method [67]. The Benson type increments for carboxylic acids esters [40] and ketones [37] (Table 2) have already been adjusted to the strain-free hydrocarbon increments [42]. We have extended the application of the strain free-increments for the acid anhydrides. In addition we define here the increment O[2CO] for the oxygen atom attached to the two carbonyl groups. Increment O[2CO]=–231.0 kJ mol^{-1} (Table 2) was calculated as the mean value from the experimental results of acetic anhydride (–228.3 kJ mol^{-1}) propanoic anhydride (–237.8 kJ mol^{-1}), and benzoic anhydride (–230.9 kJ mol^{-1}).

Table 7 Database for the calculation of the strain free increments of anhydrides (in kJ mol^{-1})

Compound	Formula	$\Delta_f H_m^o$ (*g*)/298.15 K exp.	$\Delta_f H_m^o$ (*g*) calc.	Δ
Acetic anhydride	$C_4H_6O_3$	–573.5±1.4 [3]	–576.2	2.6
Propanoic anhydride	$C_6H_{10}O_3$	–626.5±2.2 [3]	–619.7	–6.8
Isobutyric anhydride	$C_8H_{14}O_3$	(–658.4)[b]	–680.3	21.9
Pivalic anhydride	$C_{10}H_{18}O_3$	(–721.1)[c]	–739.3	18.2
Benzoic anhydride	$C_{14}H_{10}O_3$	–319.0±4.5 [10]	–318.9	–0.1
4-methylbenzoic acid anhydride	$C_{16}H_{14}O_3$	(–383.6±7.9)[d]	–383.4	–0.2
2-methylbenzoic acid anhydride	$C_{16}H_{14}O_3$	(–396.1±7.9)[e]	–383.4	–12.7

[a] Values of enthalpies of formation in brackets were not taken into account by calculation of increments. [b] Isobutyric anhydride: $\Delta_f H_m^o$ (*liq*)=–716.1 kJ mol^{-1} was calculated using enthalpy of hydrolysis $\Delta_r H_m^o$=–61.04 kJ mol^{-1} [62], $\Delta_f H_m^o$ (*liq*)=285.83±0.04 kJ mol^{-1} [46] of water, and $\Delta_f H_m^o$ (*liq*)=–531.5±1.5 kJ mol^{-1} [63] of propionic acid; enthalpy of vaporization of isobutyric anhydride was assessed using $\Delta_l^g H_m^o$=52.6±2.1 kJ mol^{-1} [3] of propanoic anhydride and the difference between enthalpies of vaporization of methyl-ethyl ketone $\Delta_l^g H_m^o$=34.92 kJ mol^{-1} [51] and methyl-iso-propyl ketone $\Delta_l^g H_m^o$=32.35 kJ mol^{-1} [51]; result: $\Delta_l^g H_m^o$=52.6+2×2.57=57.7 kJ mol^{-1}. [c] Pivalic anhydride: $\Delta_f H_m^o$ (*liq*)=–779.6±6.3 kJ mol^{-1} [3]; enthalpy of vaporization of pivalic anhydride was assessed using $\Delta_l^g H_m^o$=52.6±2.1 kJ mol^{-1} [3] of propanoic anhydride and the difference between enthalpies of vaporization of methyl-ethyl ketone $\Delta_l^g H_m^o$=34.92 kJ mol^{-1} [51] and methyl-tert-butyl ketone $\Delta_l^g H_m^o$=38.0 kJ mol^{-1} [51]; result: $\Delta_l^g H_m^o$=52.6+2×3.1=58.8 kJ mol^{-1}. [d] 4-Methylbenzoic acid anhydride: $\Delta_f H_m^o$ (*cr*)=–521.0±7.9 kJ mol^{-1} [10] and $\Delta_g^{cr} H_m^o$=137.4 kJ mol^{-1} calculated using MLRA-method [67]. [e] 2-Methylbenzoic acid anhydride: $\Delta_f H_m^o$ (*cr*)=–533.5 kJ mol^{-1} [10] and $\Delta_{cr}^g H_m^o$=137.4 kJ mol^{-1} calculated MLRA-method [67]

Mean value of increment was calculated taking into consideration the uncertainty as a statistical weighting factor [49]. We were reticent to involve the $\Delta_f H_m^0$ (g) data for 4-methylbenzoic acid anhydride and 2-methylbenzoic acid anhydride by calculation of the increment O[2CO] because of their calculated sublimation enthalpies. However, these data are very consistent with the data for other anhydrides, refer to Table 7. Isobutyric and pivalic anhydrides differ by about 20 kJ mol^{-1} from the correlation with other compounds (Table 7). These differences can be attributed to steric repulsions of the bulky substituents.

Conclusions

The group-additivity method serves as valuable tool for many scientists and engineers whose work involves thermodynamic characterisation of elementary and overall reaction processes. Improved group-additivity parameters and the correction terms were systematically revised and evaluated in this work using an updated database. The derived values can be applied to the prediction of the $\Delta_f H_m^0$ (g) of a broad range of nitrogen and oxygen containing compounds.

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