JCT



Thermochemistry of imines: experimental standard molar enthalpies of formation

Sergey P. Verevkin, ^{*a,b*} Jens Morgenthaler, and Christoph Rüchardt ^{*a*}

Institute of Organic Chemistry and Biochemistry, University of Freiburg, Albertstr. 21, D-79104 Freiburg i. Br., F.R.G.

The standard $(p^{\circ} = 0.1 \text{ MPa})$ molar enthalpies of formation $\Delta_t H_m^{\circ}(1 \text{ or cr})$ at the temperature T = 298.15 K were measured using combustion calorimetry for benzophenone-imine (A), *N*-methyl-benzaldehyde-imine (B), *N*-benzyl-benzaldehyde-imine (C), *N*-benzyl-pivalophenone-imine (D), *N*-cyclohexyl-(2,4,6-trimethyl)-benzaldehyde-imine (E), *N*-phenyl-benzaldehyde-imine (F), *N*-phenyl-4-nitro-benzaldehyde-imine (G), and *N*-phenyl-benzophenone-imine (H). The standard molar enthalpies of vaporization $\Delta_t^{\text{g}} H_m^{\circ}$ of compounds A to H were obtained from the temperature variation of the vapour pressure measured in a flow system. Molar enthalpies of fusion $\Delta_{cr}^{\text{e}} H_m^{\circ}$ of solid compounds were measured by d.s.c.

	$\frac{\Delta_{\rm f} H^{\circ}_{\rm m}({\rm l \ or \ cr})}{{\rm kJ} \cdot {\rm mol}^{-1}}$	$\frac{\Delta_{\rm cr}^{\rm l} H_{\rm m}^{\circ}}{\rm kJ} \cdot {\rm mol}^{-1}$	$\frac{\Delta_{l}^{g}H_{m}^{\circ} \text{ or } \Delta_{cr}^{g}H_{m}^{\circ}}{k\mathbf{J}\cdot\mathbf{mol}^{-1}}$	$\frac{\Delta_{\rm f} H^{\circ}_{\rm m}({\rm g})}{{\rm kJ}\cdot{\rm mol}^{-1}}$
A(1)	172.69 + 0.85		75.72 ± 0.97	248.4 + 1.3
B(l)	105.85 ± 0.83		51.22 ± 0.20	157.07 ± 0.85
C(I)	183.78 ± 0.70		85.0 ± 1.2	268.8 ± 1.4
D(cr)	46.74 ± 0.98	27.86 ± 0.21	109.7 ± 3.3	156.4 ± 3.4
E(cr)	-128.0 ± 2.0	25.61 ± 0.21	104.85 ± 0.83	-23.2 ± 2.2
F(cr)	181.6 ± 1.4	20.42 ± 0.21	98.1 ± 1.2	279.7 ± 1.8
G(cr)	137.50 ± 0.74	24.56 ± 0.21	126.0 ± 1.3	263.5 ± 1.5
H(cr)	252.5 ± 1.4	29.14 ± 0.21	119.7 ± 1.8	372.2 ± 2.3

© 1997 Academic Press Limited

KEYWORDS: enthalpy of vaporization; enthalpy of sublimation; enthalpy of formation; imine

1. Introduction

Only four imines were characterized with thermochemical data in the recent literature: the standard molar enthalpies of formation $\Delta_{\rm f} H_{\rm m}^{\circ}$ of two methaneimines and ethaneimine were derived^(1,2) by mass spectrometry, with uncertainties of about \pm (8 to 16) kJ·mol⁻¹; and the thermochemical quantities of *N*-phenyl-benzaldehyde-imine were measured by combustion calorimetry.⁽³⁾ These

0021 - 9614/97/101175 + 09 \$25.00/0/ct970242

© 1997 Academic Press Limited

^{*a*} To whom correspondence should be addressed.

^b Present address: Institute of Physical Chemistry, University of Rostock, Hermannstr. 14, 18051 Rostock, F.R.G. sergey.verevkin@chemie.uni-rostock.de



FIGURE 1. Structures of benzophenone-imine (A), *N*-methyl-benzaldehyde-imine (B), *N*-benzyl-benzaldehyde-imine (C), *N*-benzyl-pivalophenone-imine (D), *N*-cyclohexyl-(2,4,6-trimethyl)-benzaldehyde-imine (E), *N*-phenyl-benzaldehyde-imine (F), *N*-phenyl-4-nitro-benzaldehyde-imine (G), and *N*-phenyl-benzophenone-imine (H).

results are too limited to provide any reasonable insight into the energetics of imines. The present paper describes a systematic investigation of the thermochemistry of imines. The resulting standard molar enthalpies of formation in the gas state were obtained from calorimetrically measured molar enthalpies of combustion and molar enthalpies of sublimation or vaporization obtained by a transpiration method.

2. Experimental

Imines with hydrogen atoms or small alkyl groups attached to the carbon or the nitrogen atom (methaneimine, ethaneimine) are known to be unstable in the condensed phase.⁽¹⁾ This precludes the preparation of pure samples for a thermochemical investigation. We chose, therefore, for this investigation, imine molecules which were stabilized by attached phenyl substituents (figure 1).

The pure Aldrich products A, B, C, and F, each with a mass-fraction purity of about 0.99, were purified by repeated distillation under reduced pressure (A to C). To avoid traces of water in liquid samples for combustion experiments, the purified samples were dried over molecular sieves and distilled once more before combustion. Such a procedure produced a colourless material, and the absence of water was shown by Karl Fischer titration. A synthetic pathway to the molecules D, E, G, and H was successfully found following Padka *et al.*⁽⁴⁾ A mixture with equal amounts of aldehyde and amine and a catalytic amount of toluenesulfonic acid in toluene was refluxed and stirred for 24 h. Then the ctalyst was removed by washing with NaOH. The organic layer was dried over MgSO₄, and the solvent was evaporated. The

Compound	n.m.r. peak assignments
N-benzyl-pivalophenone-imine	$\delta = 1.21 \text{ ppm } (s, 9H, -CH_3), 4.23 (s, 2H, =N-CH_2),$ 7.19–7.45 (m. 6H, ArH).
N-cyclohexyl-(2,4,6-trimethyl)-benzaldehyde-imine	$\delta = 1.20-1.51$ ppm (m, 3H, >CH ₂), 1.54–1.92 (m, 7H, >CH ₂), 2.28 (s, 3H, -CH ₃), 2.36 (s, 6H, -CH ₃), 3.12–3.27 (m, 1H, =N-CH) 6.85 (s, 2H, Ar-H), 8.58 (s, 1H, -N=CH).
N-phenyl-benzaldehyde-imine	$\delta = 7.13-7.28$ ppm (m, 3H, Ar-H), 7.33-755 (m, 5H, Ar-H), 7.84-197 (m, 2H, Ar-H), 8.48 (s, 1H, =N-CH).
N-phenyl-4-nitro-benzaldehyde-imine	$\delta = 7.48 - 7.67$ ppm (m, 5H, Ar-H), 7.88-8.00 (m, 2H, Ar-H), 8.03-8.17 (m, 2H, Ar-H), 8.52 (s, 1H, -N=CH).
N-phenyl-benzophenone-imine	$\begin{split} \delta &= 6.67 - 6.80 \text{ ppm (m, 2H, Ar-H)}, \ 6.88 - 7.00 \text{ (m, } 1\text{H, Ar-H)}, \ 7.05 - 7.21 \text{ (m, 4H, Ar-H)}, \ 7.22 - 7.33 \text{ (m, 3H, Ar-H)}, \ 7.34 - 7.53 \text{ (m, 3H, Ar-H)}, \ 7.68 - 7.81 \text{ (m, 2H, Ar-H)}. \end{split}$

TABLE 1. The structures of the investigated imines established by n.m.r. spectroscopy: ¹H-n.m.r. (frequency 250 Mhz, solvent CDCl₃, and tetramethylsilane as internal standard)

compounds D to H were purified by repeated crystallization from petroleum ether (boiling temperature range 303 K to 323 K) and further sublimed under reduced pressure to remove any traces of solvent.

The structures of the compounds D, E, G, and H were established by n.m.r. spectroscopy: the n.m.r. peak assignments are shown in table 1. The degree of purity was determined by g.l.c. and by d.s.c.⁽⁵⁾ For all solid compounds, a purity greater than mass fraction 0.9990 was established by d.s.c. studies of the melting process.⁽⁵⁾ No impurities (>1 mass fraction $\cdot 10^{-4}$) could be detected in B and D to H by g.l.c. In the liquid samples A and C, mass fractions $15 \cdot 10^{-4}$ and $17 \cdot 15^{-4}$ of unidentified impurities were found by g.l.c. (no corrections were applied in the calculation of the molar enthalpies of combustion).

All compounds were handled under an inert atmosphere (N₂) using carefully dried solvents. We used the following equipment: ¹H-n.m.r., Bruker WM 250 (250 MHz), CDCl₃ solvent, and tetramethylsilane as an internal standard; G.l.c., Carlo Erba Fraktometer Vega Series GC 6000, Hewlett Packard Integrator 3390A, N₂-flow of 0.333 cm³·s⁻¹, SE-30 capillary column length 25 m. The standard temperature program of the g.l.c. was T = 363 K for 60 s, followed by a rate 0.167 K·s⁻¹ up to T = 523 K. Melting temperatures and enthalpies of fusion were determined with a Perkin-Elmer DSC-2C coupled with an Olivetti PC M 28.

For measurements of the enthalpies of combustion of substances A to H, an isoperibol macrocalorimeter with a static bomb and a stirred water bath was used. The substances were pressed into pellets of mass ≈ 400 mg or, if liquid, were placed in polyethene capsules. All substances were burned in oxygen at p = 3.05 MPa. The completeness of the combustion of the crystalline samples was ensured by the addition of about 50 mg of oil to the pellet. The preparation of the samples for combustion was carried out in a glove-box under an inert atmosphere (N₂). The detailed procedure has been described previously.^(6,7) The calorimetric bomb used in

these experiments was lined with platinum. For complete dissolution of the product gases after combustion, 0.78 g of water was added to the bomb. The energy of ignition was determined to be 1.46 J. The energy equivalent of the calorimeter ε_{calor} was determined with a standard reference sample of benzoic acid (sample SRM 39i, NIST). From eight experiments, ε_{calor} was measured to be (25112.6 \pm 1.9) J·K⁻¹. For the reduction of the data to standard conditions, conventional procedures⁽⁸⁾ were used. The corrections made for nitric acid formation were based on titration with 0.1 mol·dm⁻³ NaOH(aq). The atomic weights used were those recommended by the IUPAC Commission.⁽⁹⁾ The densities of the solid substances were determined by submerging pellets of the substances in water in a calibrated 10 cm³ pycnometer. The densities of the liquid compounds were taken from the Aldrich catalog. The massic heat capacities and enthalpies of fusion were measured with the d.s.c. A summary of auxiliary quantities for the combustion experiments and information necessary for reducing apparent mass to mass is given in table 2.

The enthalpies of vaporization of compounds A to C, and the enthalpies of sublimation of compounds D to H, were determined from their equilibrium vapour pressures, which were measured on the basis of the amount of the gaseous compounds transported in a well-defined nitrogen stream.⁽¹⁰⁻¹²⁾ The substances were mixed with glass beads and placed in a thermostatted U-tube. At each of several different temperatures, a nitrogen stream was passed through the U-tube, the transported material was collected in a cold trap, and its amount was determined by g.l.c. analysis using an internal standard. The vapour pressure *p* at the saturation temperature was calculated from the amount of condensed product collected within a definite time, and the residual vapour pressure at condensation temperature was taken into account. The latter was calculated from a linear correlation between $\ln[(m/m^{\circ})/{V(N_2)/V^{\circ}}]$ against T^{-1} obtained by iteration, where *m* is the

	$rac{T_{ ext{fus}}^a}{ ext{K}}$	$\frac{\Delta^{1}_{\rm cr}H^{\circ \ a}_{\rm m}}{\rm kJ{\cdot}mol^{-1}}$	$\frac{\rho(293 \text{ K})}{\text{g} \cdot \text{cm}^{-3}}$	$\frac{c_p(298.15 \text{ K})^{a}}{\text{J} \cdot \text{K}^{-1} \text{ g}^{-1}}$	$\frac{10^{-6} \cdot (\delta v_{\rm m}/\delta T)_p}{\rm dm^{-3} \cdot K^{-1}}$
benzophenone-imine			1.080	1.84	1.0
N-methyl-benzaldehyde-imine			0.967	1.38	1.0
N-benzyl-benzaldehyde-imine			1.038	1.97	1.0
N-benzyl-pivalophenone-imine	339.55	27.86	1.02	2.34	0.1
<i>N</i> -cyclohexyl-(2,4,6-trimethyl)-benzaldehyde-imine	339.35	25.61	1.13	1.72	0.1
N-phenyl-benzaldehyde-imine	329.65	20.42	1.09	1.67	0.1
N-phenyl-4-nitro-benzaldehyde-imine	347.15	24.56	1.15	1.76	0.1
N-phenyl-benzophenone-imine	392.25	29.14	1.12	1.67	0.1
oil ^d			$0.880^{(6)}$	$0.84^{(6)}$	1.0
cotton ^e			1.500(6)	1.67(6)	0.1
polyethene ^f			0.920	2.53	0.1

TABLE 2. Temperature T_{fus} and standard molar enthalpy of fusion $\Delta_{\text{cr}}^{\text{l}}H_{\text{m}}^{\text{o}}$, density $\rho(293 \text{ K})$, massic heat capacity $c_{\rho}(298.15 \text{ K})$, and expansion coefficients $(\delta v_{\text{m}}/\delta T)_{\text{p}}$ of the materials used in present study

^{*a*} From d.s.c. measurements; the usual error bars of $\Delta_{cr}^{1}H_{m}^{\circ}$ measurements are ± 0.21 kJ·mol⁻¹. ^{*b*} Measured with the pycnometer only for solids; for liquids, densities from the Aldrich catalog were used. ^{*c*} Estimated. ^{*d*} From nine combustion experiments, $\Delta_{c}u^{\circ}(CH_{1.940}) = -(46003.6 \pm 4.0)$ J·g⁻¹. ^{*e*} From 10 combustion experiments, $\Delta_{c}u^{\circ}(CH_{1.74}O_{0.887}) = -(16945 \pm 4.2)$ J·g⁻¹) J·g⁻¹. ^{*f*} From 11 combustion experiments, $\Delta_{c}u^{\circ}(CH_{1.930}) = -(46361.0 \pm 3.1)$ J·g⁻¹.

mass of transported compound; $m^{\circ} = 1 \text{ mg}$; $V(N_2)$ is the volume of transporting gas; and $V^{\circ} = 1 \text{ dm}^3$. The molar enthalpies of vaporization or sublimation were calculated from the slope of the linear correlation:

$$\Delta_{\rm I}^{\rm g} H_{\rm m}^{\circ} = -R \big({\rm dln}[(m/m^{\circ})/\{V({\rm N}_2)/V^{\circ}\}]/{\rm d}T^{-1} \big), \tag{1}$$

with $R = 8.31451 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The observed enthalpies of vaporization $\Delta_{i}^{g}H_{m}^{\circ}(T)$ or sublimation $\Delta_{cr}^{g}H_{m}^{\circ}(T)$ obtained by this procedure are listed in table 3.

3. Results and discussion

The results for a typical combustion experiment on each compound are given in table 4. The individual values of the standard massic energy of combustion $\Delta_c u^\circ$, together with the mean and its standard deviation, are given in table 5. To derive $\Delta_t H^\circ_m$ from $\Delta_c H^\circ_m$ the following molar enthalpies of formation were used:⁽⁹⁾ for H₂O(l), $-(285.83 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$; and for CO₂(g), $-(393.51 \pm 0.13) \text{ kJ}\cdot\text{mol}^{-1}$.

TABLE 3. Results from measurements of the vapour pressure p by the transpiration method^(11, 12)

$T/{ m K}$ a	$m/{ m mg}~^b$	$V(N_2)/dm^{3 c}$	$p/\mathbf{P}\mathbf{a}^{\ d}$	$T/{ m K}$ a	$m/{ m mg}$ b	$V(\mathrm{N_2})/\mathrm{dm^{3~c}}$	$p/\mathrm{Pa}^{\ d}$
			benzophe	none-imine			
308.5 314.3 318.5 323.6	1.04 1.54 0.987 0.987	30.52 28.05 11.62 7.81	0.486 0.752 1.161 1.726	328.5 333.2 338.3	1.15 1.22 1.35	5.80 4.15 3.20	2.712 4.025 5.769
		$\Delta^{ extsf{g}}_{ extsf{l}} H^{\circ}_{ extsf{m}}(3) \ \Delta^{ extsf{g}}_{ extsf{l}} H^{\circ}_{ extsf{m}}(2)$	(23.4 K) = (7) (4.21 ± 0.97) 1 75.72 ± 0.97)	kJ·mol ^{−1} kJ·mol ^{−1}		
		Λ	-methyl-ben	zaldehyde-imi	ine		
283.4 288.5 293.6 298.4	4.95 6.00 5.68 7.67	4.22 3.43 2.22 2.12	25.84 37.84 54.65 76.69	303.6 308.4 313.3 318.3	7.75 5.26 3.38 2.43	1.52 0.747 0.343 0.182	107.5 147.9 206.4 278.6
		$\Delta_{\rm I}^{\rm g} H_{\rm m}^{\rm o}(3)$ $\Delta_{\rm I}^{\rm g} H_{\rm m}^{\rm o}(2)$	(00.9 K) = (5) (38.15 K) = (5)	$1.06 \pm 0.20)$ 1 51.22 $\pm 0.20)$	kJ·mol ^{−1} kJ·mol ^{−1}		
		Λ	/-benzyl-benz	zaldehyde-imi	ine		
308.5 313.5 314.3 318.5 323.6	0.397 0.602 0.748 0.436 0.517	34.03 30.40 32.59 12.95 8.88	0.1482 0.2511 0.2910 0.4274 0.7385	326.5 328.5 333.2 338.3 339.5	0.504 0.602 0.660 0.748 0.534	6.80 6.47 4.63 3.57 2.41	0.9408 1.180 1.808 2.656 2.808
		$\Delta^{g}_{I}H^{\circ}_{m}(2)$	(324.0 K) = (83.4 ± 1.2) k. (85.0 ± 1.2) l	$J \cdot mol^{-1}$		
		Δ ₁ Πm(2	-benzyl-nival	ophenone-im	ine		
318.4 323.2 328.2	2.39 4.17 6.53	117.6 107.0 99.11	0.2006 0.3848 0.6493	333.2 336.5	6.36 5.06	47.47 28.18	1.320 1.769

			TIBLE 5	commucu			
<i>T</i> /K ^{<i>a</i>}	m/mg ^b	$V(N_2)/dm^{3 c}$	p/Pa^{d}	T/K^{a}	m/mg ^b	$V(N_2)/dm^{3 c}$	p/Pa^{d}
		$\Delta^{ ext{g}}_{ ext{cr}} H^{\circ}_{ ext{m}} (\Delta^{ ext{g}}_{ ext{cr}} H^{\circ}_{ ext{m}})$	(327.5 K) = (10) (327.5 K) = (10)	$07.9 \pm 3.3)$ H 09.7 ± 3.3 H	cJ·mol ^{−1} cJ·mol ^{−1}		
		Λ	-benzyl-pivalo	phenone-im	ine		
341.3	4.95	17.91	2.728	357.1	1.78	1.91	9.192
346.3 352.6	4.95 3.08	4.58	3.926 6.637	361.5 366.1	2.16 2.45	1.71	12.45 17.65
		$\Delta^{ extsf{g}}_{ extsf{l}} H^{\circ}_{ extsf{m}}(2) \ \Delta^{ extsf{g}}_{ extsf{l}} H^{\circ}_{ extsf{m}}(2)$	(353.7 K) = (78) (98.15 K) = (8)	$.31 \pm 0.85)$ $1.64 \pm 0.85)$	kJ∙mol ^{−1} kJ∙mol ^{−1}		
		N-cyclohex	yl-(2,4,6-trime	thyl)-benzal	dehyde-imin	ie	
318.2	0.982	52.59	0.2019	331.3	1.36	15.59	0.9414
323.6 328.4	1.46 2.44	41.82 38.98	0.3766 0.6759	336.1	0.516	3.50	1.592
02011	2	$\Delta^{\rm g}_{ m cr} H^{\circ}_{ m m}(3)$ $\Delta^{\rm g}_{ m cr} H^{\circ}_{ m m}(2)$	(27.2 K) = (10) (98.15 K) = (10)	$3.11 \pm 0.83)$ $4.85 \pm 0.83)$	kJ·mol ^{−1}) kJ·mol ^{−1}		
		N-cyclohex	yl-(2,4,6-trime	thyl)-benzal	dehyde-imin	e	
341.4	0.505	2.27	2.404	358.2	0.835	1.09	8.283
348.2 353.5	$0.788 \\ 0.699$	2.02 1.26	4.215 5.998	363.4 368.5	$0.680 \\ 0.779$	$0.600 \\ 0.490$	12.25 17.19
		$\Delta^{\mathrm{g}}_{\mathrm{I}} H^{\circ}_{\mathrm{m}}(2)$ $\Delta^{\mathrm{g}}_{\mathrm{I}} H^{\circ}_{\mathrm{m}}(2)$	355.0 K) = (75 98.15 K) = (78	3.30 ± 0.95	kJ·mol ^{−1} kJ·mol ^{−1}		
			V-phenyl-benz	aldehyde-im	ine		
293.5	1.36	442.9	0.04183	316.7	2.22	34.87	0.8686
298.6 302.4	1.32	205.8	0.08763	318.4	4.76	60.98 12.42	1.066
307.5	2.79	139.3	0.2740	321.2	5.31	48.73	1.490
312.6	2.73	69.35	0.5384	326.2	5.02	30.03	2.282
		$\Delta^{ ext{g}}_{ ext{cr}} H^{\circ}_{ ext{m}} \ \Delta^{ ext{g}}_{ ext{cr}} H^{\circ}_{ ext{m}} ($	(309.9 K) = (9) (298.15 K) = (9)	97.4 ± 1.2) k 98.1 ± 1.2) k	J·mol ^{−1} cJ·mol ^{−1}		
		N-pł	nenyl-4-nitro-b	enzaldehyde	e-imine		
359.2	1.19	41.10	0.3178	377.7	1.30	9.32	1.530
368.3	1.52	24.45	0.6823	386.9	1.69	5.79	3.194
372.8	1.80	18.15	1.086				
		$\Delta^{ extsf{g}}_{ extsf{l}} H^{\circ}_{ extsf{m}} (2) \ \Delta^{ extsf{g}}_{ extsf{l}} H^{\circ}_{ extsf{m}} (2)$	(373.1 K) = (9) (298.15 K) = (1)	6.9 ± 1.3) k 01.4 ± 1.3)	J∙mol ⁻¹ kJ∙mol ⁻¹		
		Λ	-phenyl-benzo	phenone-im	ine		
348.1	1.02	81.67	0.1205	372.8	3.23	18.62	1.670
352.9 359.2	1.98	83.50 42.18	0.2286	377.7 382.7	2.77	9.57 7.70	2.791
363.6	3.01	47.53	0.6106	386.9	4.12	5.94	6.675
368.3	2.61	25.09	1.000	1551101	T 1 1		
		$\Delta^{\scriptscriptstyle{5}}_{\mathrm{cr}} H^{\scriptscriptstyle{0}}_{\mathrm{m}}(Z)$	(30/.5 K) = (1) 298.15 K) = (1	$15.5 \pm 1.8)$ 19.7 ± 1.8)	kJ·mol ^{−1} kJ·mol ^{−1}		

TABLE 3—continued

^{*a*} Temperature of saturation, N₂ gas flow (0.26 to 0.52) cm³·s⁻¹ by each run of saturation. ^{*b*} Mass of transferred sample condensed at T = 243 K. ^{*c*} Volume of nitrogen used to transfer sample. ^{*d*} Vapour pressure at temperature T of experiment; corrections for residual vapour pressure at T = 243 K were made.

TABLE	Ξ4.	Res	Its from typical combustion experiments at $T = 298.15 \text{ K}$ ($p^{\circ} = 0.1 \text{ MPa}$), when	re
A =	ben	zopł	none-imine, $B = N$ -methyl-benzaldehyde-imine, $C = N$ -benzyl-benzaldehyde	э-
imine,	D	=	N-benzyl-pivalophenone-imine, $E = N$ -cyclohexyl-(2,4,6-trimethyl)-benzaldehydd	e -
imine,	F	=	N-phenyl-benzaldehyde-imine, $G = N$ -phenyl-4-nitro-benzaldehyde-imine, an	d
			H = N-phenyl-benzophenone-imine ^{<i>a</i>}	

	А	В	С	D
<i>m</i> (substance)/g ^b	0.684844	0.392126	0.744186	0.600494
$m'(\text{cotton})/g^{b}$	0.001057	0.001070	0.001033	0.000894
$m''(oil)/g^{b}$				0.045788
m'''(polyethene)/g ^b	0.266933	0.273294	0.271073	
$\Delta T_{\rm c}/{\rm K}^{2}$	1.52642	1.10077	1.64770	1.04807
$\varepsilon_{\rm calor} \cdot (-\Delta T_{\rm c})/{\rm J}$	-38332.39	-27643.24	-41377.98	-26319.86
$\varepsilon_{\rm cont} \cdot (-\Delta T_{\rm c})/{\rm J}$	-21.59	-15.34	-23.66	-14.32
$\Delta U_{\rm corr}/{\rm J}$	20.36	11.65	21.74	12.77
$-m'\Delta_c u'/J^d$	17.91	18.13	17.50	15.14
$-m''\Delta_c u''/\mathbf{J}^d$				2106.43
$-m'''\Delta_c u'''/J^d$	12375.29	12670.16	12567.21	
$\Delta U(HNO_3)/J$	38.51	31.35	40.00	26.27
$\Delta_{\rm c} u^{\circ}({\rm sub})/({\rm J}\cdot{\rm g}^{-1})$	-37819.5	- 38063.9	-38637.8	-40253.7
	Е	F	G	Н
<i>m</i> (substance)/g ^b	0.368441	0.481974	0.435449	0.547545
$m'(\text{cotton})/g^{b}$	0.000841	0.001023	0.000906	0.000881
$m''(oil)/g^{b'}$	0.059312	0.065000	0.047526	0.062338
m'''(polyethene)/g ^b				
$\Delta T_{\rm c}/{\rm K}^{\rm c}$	0.71361	0.84800	0.60095	0.95164
$\varepsilon_{\rm calor} \cdot (-\Delta T_{\rm c})/{\rm J}$	-17920.48	-21295.48	-15091.28	-23898.08
$\varepsilon_{\rm cont} \cdot (-\Delta T_{\rm c})/{\rm J}$	-9.21	-11.08	-7.86	-13.02
$\Delta U_{ m corr}/ m J$	7.03	11.42	9.29	13.42
$-m'\Delta_{\rm c}u'/{ m J}$ d	14.24	17.33	15.35	14.92
$-m''\Delta_{\rm c}u'''/{\bf J}^{d}$	2728.56	2990.23	2186.39	2867.76
$-m'''\Delta_{c}u'''/J^{d}$				
$\Delta U(HNO_3)/J$	18.51	25.08	29.55	22.09
$\Delta_{\rm c} u^{\circ}({\rm sub})/({\rm J}\cdot{\rm g}^{-1})$	-41146.1	-37888.0	-29526.1	-38337.4

^{*a*} For the definition of the symbols see reference 8: $T_h = 298.15 \text{ K}$; $V(\text{bomb}) = 0.2664 \text{ dm}^3$; $p^i(\text{gas}) = 3.05 \text{ MPa}$; $m^i(\text{H}_2\text{O}) = 0.78 \text{ g}$; $\Delta U(\text{ign}) = 1.5 \text{ J}$; m(Pt) = 12.18 g. ^{*b*} Masses obtained from apparent masses. ^{*c*} $\Delta T_c = (T^f - T^i + \Delta T_{\text{corr}})$; $\varepsilon_{\text{calor}} = (25112.6 \pm 1.9) \text{ J} \cdot \text{K}^{-1}$; $\varepsilon_{\text{cont}} \cdot (-\Delta T_c) = (\varepsilon^i_{\text{cont}}) \cdot (T^i - 298.15 \text{ K}) + (\varepsilon^i_{\text{cont}}) \cdot (298.15 \text{ K} - T^f + \Delta T_{\text{corr}})$. ^{*d*} ΔU_{corr} , the correction to standard states, is the sum of items 81 to 85, 87 to 90, 93, and 94 in reference 8.

The enthalpies of vaporization $\Delta_{\rm f}^{\rm g} H_{\rm m}^{\circ}$ or sublimation $\Delta_{\rm gr}^{\rm g} H_{\rm m}^{\circ}$ at T = 298.15 K are recorded in table 6. Because the temperature range of the vapour pressure measurements was usually above T = 298.15 K the enthalpies of vaporization or sublimation had to be corrected to this reference temperature. The corrections were estimated with the help of the "Sidgwick correction": $\{\Delta_{\rm gr}^{\rm g} H_{\rm m}^{\circ}(\langle T \rangle) - \Delta_{\rm cr}^{\rm g} H_{\rm m}^{\circ}(298.15 \text{ K})\}/(\text{kJ}\cdot\text{mol}^{-1}) = -6\cdot10^{-2}\cdot\{\langle\langle T \rangle/\text{K}\rangle - 298.15\},$ following the recommendation of Chickos *et al.*⁽¹³⁾ With these corrections, and the measured values of $\Delta_{\rm f}^{\rm g} H_{\rm m}^{\circ}(T)$ and $\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\circ}(T)$ from table 3, the standard molar enthalpies of vaporization or sublimation at T = 298.15 K wre calculated (tables 3 and 6). Table 6 also lists the standard molar enthalpies of combustion, and standard

TABLE 5. Values of massic energies of combustion $\Delta_c u^\circ$ at T = 298.15 K ($p^\circ = 0.1$ MPa) for imines: A = benzophenone-imine; B = N-methyl-benzaldehyde-imine; C = N-benzyl-benzaldehyde-imine; D = N-benzyl-pivalophenone-imine; E = N-cyclohexyl-(2,4,6-trimethyl)-benzaldehyde-imine; F = N-phenyl-benzaldehyde-imine; G = N-phenyl-4-nitro-benzaldehyde-imine; and H = N-phenyl-benzophenone-imine

_					-					
	А	В	С	D	Е	F	G	Н		
$-\Delta_{c}u^{\circ}/(\mathbf{J}\cdot\mathbf{g}^{-1})$										
	37819.5 37829.8 37812.8 37824.9	38051.2 38063.9 38055.8 38079.2	38637.2 38637.8 38631.5 38630.7	40258.6 40253.7 40250.6 40261.0	41146.1 41181.9 41160.2 41175.5	37888.0 37860.2 37861.9 37856.1 37888.4	29526.1 29536.2 29528.3 29533.8	38337.4 38322.0 38334.8 38342.0		
				$\langle -\Delta_{\rm c} u^{\circ} \rangle$	$\langle (\mathbf{J} \cdot \mathbf{g}^{-1}) a \rangle$					
	$\begin{array}{r} 37821.8 \\ \pm 3.7 \end{array}$	$38062.5 \\ \pm 6.2$	$\begin{array}{r} 38634.3 \\ \pm 1.9 \end{array}$	40256.0 ± 2.4	41165.9 ±8.0	$\begin{array}{r} 37870.9 \\ \pm 7.1 \end{array}$	$\begin{array}{r} 29531.0 \\ \pm 2.4 \end{array}$	$38334.1 \\ \pm 4.3$		

^{*a*} Mean value and uncertainty interval of $\Delta_c u^\circ$.

molar enthalpies of formation in the condensed and gaseous states. The given standard deviations of the mean include the uncertainties from calibration and the combustion energies of the auxiliary materials.

The thermochemical properties of substances A to E and G to H were determined for the first time. Only the enthalpy of formation $\Delta_f H_m^{\circ}(cr) = (167.8 \pm 7.1) \text{ kJ} \cdot \text{mol}^{-1}$ of *N*-phenyl-benzaldehyde-imine (F) had been measured earlier by Coates and Sutton,⁽³⁾ using combustion calorimetry. The reported value is 13.8 kJ·mol⁻¹ more negative than that determined in this work, but due to the error limit of $\pm 7.1 \text{ kJ} \cdot \text{mol}^{-1}$, both measurements are in acceptable agreement. The enthalpy of sublimation of F, (98.1 \pm 1.2) kJ·mol⁻¹, however, is significantly different from the value (85.8 \pm 2.1) kJ·mol⁻¹ of Coates and Sutton.⁽³⁾

The investigation of the compounds A to H covered a broad range of structures of imines. The resulting standard enthalpies of formation fill the gap of available thermochemical data for imines and provide data to use in the calculation of the thermochemical properties of compounds with similar structures.

TABLE 6. Thermochemical results at $T = 298.15 \text{ K} (p^{\circ} = 0.1 \text{ MPa})$

	State	$\frac{-\Delta_{\rm c}H_{\rm m}^{\circ}(\rm l~or~cr)^{\rm a}}{\rm kJ{\cdot}mol^{\rm -1}}$	$\frac{\Delta_{\rm f} H_{\rm m}^{\circ}(\rm l \ or \ cr)}{\rm kJ \cdot mol^{-1}}$	$\frac{\Delta_{\scriptscriptstyle 1}^{\scriptscriptstyle {\rm g}} H_{\scriptscriptstyle \rm m}^{\scriptscriptstyle \circ \ b}}{\rm kJ{\cdot}mol^{\scriptscriptstyle -1}}$	$\frac{\Delta_{\rm cr}^{\rm g} H_{\rm m}^{\circ \ b}}{\rm kJ{\cdot}mol^{-1}}$	$\frac{\Delta_{\rm f} H^{\circ}_{\rm m}(g)}{\rm kJ{\cdot}mol^{-1}}$
benzophenone-imine	1	6860.37 ± 0.85	172.69 ± 0.85	75.72 ± 0.97		248.4 ± 1.3
N-methyl-benzaldehyde-imine	1	4540.16 ± 0.83	105.85 ± 0.83	51.22 ± 0.20		157.07 ± 0.85
N-benzyl-benzaldehyde-imine	1	7550.80 ± 0.70	183.78 ± 0.70	85.0 ± 1.2		268.8 ± 1.4
N-benzyl-pivalophenone-imine	cr	10131.20 ± 0.98	46.74 ± 0.98	81.64 ± 0.85 °	109.7 ± 3.3 ^d	156.4 ± 3.4
N-cyclohexyl-(2,4,6-trimethyl)-benzaldehyde-imine	cr	9455.2 ± 2.0	-128.0 ± 2.0	78.71 ± 0.95 °	104.85 ± 0.83 ^d	-23.2 ± 2.2
N-phenyl-benzaldehyde-imine	cr	6869.3 ± 1.4	181.6 ± 1.4		98.1 ± 1.2	279.7 ± 1.8
N-phenyl-4-nitro-benzaldehyde-imine	cr	6682.26 ± 0.74	137.50 ± 0.74	101.4 ± 1.3 ^c	126.0 ± 1.3 °	263.5 ± 1.5
N-phenyl-benzophenone-imine	cr	9872.9 ± 1.4	252.5 ± 1.4		119.7 ± 1.8	372.2 ± 2.3

^{*a*} Calculated from the massic energies of combustion in table 5. ^{*b*} From the measurements of vapour pressures at different temperatures (table 3) using the Clausius–Clapeyron equation. ^{*c*} Measured above the melting temperature. ^{*d*} Taken into account in the estimation of $\Delta_t H_m^{\circ}$ (g). ^{*c*} Enthalpy of sublimation $\Delta_x^{t} H_m^{\circ}$ calculated as the sum of $\Delta_t^{s} H_m^{\circ}$ (this table) and $\Delta_u^{L} H_m^{\circ}$ (table 2).

Thanks are due to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support. Thanks are also due to F. Schillinger and E. Hickl for technical assistance and to Dr H.-D. Beckhaus for his advice.

REFERENCES

- Peerboom, R. A. L.; Ingemann, S.; Nibbering, N. M. M.; Liebman, J. F. J. Chem. Soc. Perkin Trans. 2 1990, 1825–1828.
- 2. Holmes, J. L.; Lossing, F. P.; Mayer, P. M. Chem. Phys. Lett. 1992, 198, 211-213.
- 3. Coates, G. E.; Sutton, L. E. J. Chem. Soc. 1948, 1187-1191.
- 4. Padka, A.; Bergmark, N.; Pashayan, D. J. Am. Chem. Soc. 1969, 91, 2653-2660.
- 5. Hemminger, W. F.; Cammenga, H. K. Methoden der Thermischen Analyse. Springer: Berlin. 1989, p. 269.
- Beckhaus, H.-D.; Kratt, G.; Lay, K.; Geiselmann, J.; Rüchardt, C.; Kitschke, B.; Lindner, H. J. Chem. Ber. 1980, 113, 3441–3455.
- 7. Verevkin, S. P.; Beckhaus, H.-D.; Rüchardt C. Thermochim. Acta 1990, 197, 27-39.
- 8. Hubbard, W. N.; Scott, D. W.; Waddington, G. *Experimental Thermochemistry*. Rossini, F. D.: editor. Interscience: New York. **1956**, pp. 75–127.
- 9. CODATA Key Values for Thermodynamics. Cox, J. D.; Wagman, D. D.; Medvedev, V. A.: editors. Hemisphere: New York. 1989.
- 10. Cox, J. D.; Pilcher, G. Thermochemistry of Organic Compounds. Academic: London. 1970.
- 11. Flamm-ter Meer, M. A.; Beckhaus, H.-D.; Rüchardt, C. Thermochim. Acta 1985, 80, 81-89.
- Chickos, J. S.; Hesse, D. G.; Hosseini, S.; Liebman, J. F.; Mendenhall, G. D.; Verevkin, S. P.; Rakus, K.; Beckhaus, H.-D.; Rüchardt, C. J. Chem. Thermodynamics 1995, 27, 693–705.
- Chickos, J. S.; Hesse, D. G.; Panshin, S. Y.; Rogers, D. W.; Saunders, M.; Uffer, P. M.; Liebman, J. F. J. Org. Chem. 1992, 57, 1897–1902.

(Received 31 January 1997, in final form 15 April 1997)

O-663