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INTERRELATIONS OF THE ENERGETICS OF AMIDES AND ALKENES: ENTHALPIES OF FORMATION OF *N,N*-DIMETHYL DERIVATIVES OF PIVALAMIDE, 1-ADAMANTYLCARBOXAMIDE AND BENZAMIDE, AND OF STYRENE AND ITS α-, *TRANS*-β- AND β,β-METHYLATED DERIVATIVES

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The enthalpies of formation of the condensed phase and gaseous *N,N*-dimethyl derivatives of pivalamide, 1-adamantylcarboxamide and benzamide were determined by combustion calorimetry and the associated enthalpies of vaporization and sublimation. The enthalpies of formation of styrene and its α-, *trans*-β- and β,β-methylated derivatives were determined from measurements of their enthalpies of hydrogenation in dilute hydrocarbon solution. Strain and resonance effects of amides and alkenes are discussed in terms of the exo-/endothermicity of the following reactions:

$$CH_3CONH_2(g) + RC(CH_3){=}CH_2 \rightarrow (CH_3)_2C{=}CH_2(g) + RCONH_2(g)$$

$$CH_3CON(CH_3)_2(g) + RCH{=}C(CH_3)_2(g) \rightarrow CH_3CH{=}C(CH_3)_2(g) + RCON(CH_3)_2(g)$$

and in terms of the difference of enthalpies of formation of the isomeric (*Z*)- and (*E*)-$RCH{=}CHCH_3$.

1. INTRODUCTION

The current study arises from the confluence of our earlier but independent, studies that were designed to (1) determine the enthalpies of combustion, and therefore of formation, of carbonyl and thiocarbonyl compounds,[1] so that one can quantitatively assess strain effects to understand proton reactivity; (2) determine the enthalpies of hydrogenation, and therefore of formation, of acyclic and cyclic alkenes,[2] so that one can quantitatively assess strain effects to understand the various modes of conjugation and aromaticity; and (3) understand the energetics of the resonance stabilized, but otherwise seemingly 'normal' amides in terms of other 'normal' species, especially alkenes.[3]

In this paper, we report a study of thermochemical

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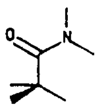

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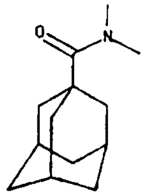

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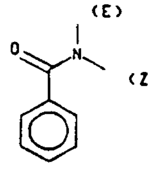

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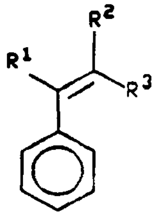

4a $R^1=R^2=R^3=H$
4b $R^1=CH_3\ R^2=R^3=H$
4c $R^1=R^3=H\ R^2=CH_3$
4d $R^1=H\ R^2=R^3=CH_3$

properties of *N,N*-dimethylpivalamide (*N,N*-dimethyl-*tert*-butylcarboxamide) (lq, g) (**1**), *N,N*-dimethyl-1-adamantylcarboxamide (cr, g) (**2**) and *N, N*-dimethylbenzamide (cr, g) (**3**), where we use cr, lq and g to denote a solid purified by crystallization, liquid and gas, respectively. Purity and phase transitions over the whole working temperature range for these latter solid amides and heat capacities were determined by differential scanning calorimetry (DSC). The enthalpies of combustion were determined by direct oxygen bomb combustion calorimetry. Vapour pressures were measured over a 18 K temperature interval by the Knudsen effusion technique. The enthalpy of vaporization was determined by vaporization calorimetry. From these results, the standard molar enthalpies of combustion, sublimation and vaporization and formation in the condensed and gaseous states at 298·15 K, were derived for these three amides.

We also report the enthalpies of hydrogenation (in dilute hexane solution) of the phenylalkenes: styrene (**4a**) and its α-methyl (**4b**), *trans*-β-methyl (**4c**) and β,β-dimethyl (**4d**) derivatives. Following the earlier protocol and assumptions,[2] no phase change (here, only vaporization) enthalpies were deemed necessary for these alkenes. It was assumed that results from dilute hydrocarbon solution are equivalent to those in the gas phase to within a thermochemical accuracy[4] of about ±2·5 kJ mol^{-1}.

EXPERIMENTAL

Carboxamides

N,N-Dimethylpivalamide, (*N, N*-dimethyl-*tert*-butylcarboxamide) and *N,N*-dimethyl-1-adamantylcarboxamide were obtained by reaction of dry dimethylamine and the corresponding acid chlorides in dry diethyl ether solution. The former was purified by heating at reflux with calcium hydride in diethyl ether and then distilling *in vacuo*. The latter amide was purified by several recrystallizations from hexane. Structures were confirmed by ^{1}H NMR and IR spectra.

The purity of *N,N*-dimethylpivalamide, *N,N*-dimethyl-1-adamantylcarboxamide and (commercially available, from Aldrich Chemie) *N,N*-dimethylbenzamide were established by means of ^{1}H NMR spectrometry gas–liquid and thin-layer chromatography and mass spectrometry. The high degree of purity of the solid amides was further confirmed by DSC by the fractional fusion technique[5a], and indicated that the mole fraction of impurities was <0·002. The temperature scale of the DSC was calibrated by measuring the melting points of the recommended high-purity standards: *n*-pentadecane, *n*-octadecane, gallium, indium, tin, *n*-octadecanoic acid and benzoic acid.[5b] The power scale was calibrated using high-purity indium (>99·999 mol%) as standard material.

The combustion experiments were performed with a static bomb calorimeter, following the apparatus and procedure described previously.[6] The energies of combustion of the compounds were determined by burning the samples in oxygen, with 1 cm^3 of water added. The liquid samples for combustion were contained in sealed polythene bags made by cutting out suitably shaped pieces of polythene film and heat sealing the edges, as described by Good and Scott.[7] The solid *N,N*-dimethyl-1-adamantylcarboxamide and *N,N*-dimethylbenzamide were burnt in pellet form. The combustion bomb was flushed and filled with oxygen, previously freed from combustible impurities, up to a pressure of 3·04 MPa at 298·15 K. The initial temperature of the combustion experiments was 296·15 K. The energy of reaction was always referred to the final temperature.

NBS sample 39i benzoic acid was used for calibration. Its specific energy of combustion is [26434 ± 3] J g^{-1} under certificate conditions. The value of the energy equivalent of the calorimeter used in computing the combustion experiments was $\varepsilon(\text{calor.}) = 14{\cdot}2685 \pm 0{\cdot}0004$ kJ K^{-1}. The specific energy of combustion and empirical formula of polyethene[8] are -46371 ± 4 J g^{-1} and $C_{0{\cdot}961}H_{2{\cdot}000}$. The corrections for nitric acid formation were based on $-59{\cdot}7$ kJ mol^{-1} for the molar energy of formation of 0·1 mol d^{-3} HNO_3(aq.) from N_2, O_2 and H_2O(lq). For the correction of weighings in air to masses *in vacuo*, conversion of the energy of the actual bomb process to that of the isothermal process and correction to standard states, we used the values of density (ρ), heat capacity (C_p) and $(\delta u/\delta p^0)_T$ presented in Table 1.

Densities were measured as follows: for the crystalline *N,N*-dimethyl-1-adamantylcarboxamide and *N,N*-dimethylbenzamide, by weighing pellets of known

Table 1. Physical properties at 296·15 K (values in parentheses were estimated)

Compound	M (g mol^{-1})	ρ (g cm^{-3})	$(\delta u/\delta p)_T$ (J kPa^{-1} g^{-1})	C_p (J K^{-1} g^{-1})
Polyethene	13·558	0·918	(−0·00023)	2·0
N,N-Dimethyl-*tert*-butylcarboxamide	129·202	0·90	(−0·00027)	1·95
N,N-Dimethyl-1-adamantylcarboxamide	207·315	1·18	(−0·00012)	1·24
N,N-Dimethylbenzamide	149·192	1·11	(−0·00023)	1·34

volume, and of the liquid *N,N*-dimethylpivalamide by direct determination. Heat capacities were determined by DSC. Correction to standard states (standard pressure $p^0 = 101{\cdot}325$ kPa) were made according to Hubbard *et al.*[9a] The molar masses of the elements were the 1979 recommendations of IUPAC.[9b]

The vapor pressures were measured by the Knudsen effusion method using the procedure described previously.[10] The apparatus consisted, essentially, of a stainless-steel sublimation chamber immersed in a jacket and connected to a high-vacuum system (1×10^{-4} Pa). The temperature of the jacket was maintained constant to within ±0·005 K for each vapor pressure experiment, and measured with a calibrated platinum resistance thermometer. The enthalpies of sublimation were computed from relationships between pressure and temperature. The details of the effusion orifice employed in our sublimation experiments are as follows: orifice area $(6{\cdot}69 \pm 0{\cdot}01) \times 10^{-3}$ cm^2 and Clausing coefficient, $W_a = 0{\cdot}986 \pm 0{\cdot}003$ for *N,N*-dimethyl-1-admantylcarboxamide, and orifice area $(3{\cdot}47 \pm 0{\cdot}02) \times 10^{-3}$ cm^2 and Clausing coefficient $W_a = 0{\cdot}980 \pm 0{\cdot}004$ for *N,N*-dimethylbenzamide. The measurements of enthalpy of vaporization were done using a Wadsö calorimeter, using the apparatus and procedure extensively described by Wadsö[11] and calibrated by measurements of the enthalpy of vaporization of water.[12]

Styrenes

Following the details given elsewhere,[2,13] about 100 mg of the parent or particular methylated styrene were weighed to ±0·002 mg and diluted to 400 μl in an ultraprecision graduated NMR tube which we had cut to size for the purpose. A thermochemically equivalent amount of standard was weighed and diluted in the same way. Thermochemical equivalency means that the amount of standard taken was calculated to give roughly the same heat output as the 'unknown' (based on a previous experiment, molecular mechanics calculation or a guess). Aliquot portions of 20 μl of the unknown and standard solutions were injected, alternately, into a solution calorimeter containing a hexane catalyst that was stirred magnetically. This produced a series of ratios of reaction enthalpy of the unknown to the standard (q_u/q_s). Knowing the molar ratio of unknown to standard, and the enthalpy of hydrogenation (ΔH_h) of the standard permits calculation of the ΔH_h of the unknown. After the first experimental run for a given compound, estimation of thermochemical equivalency should be fairly accurate. The actual experiment consists in determining by how much the real system differs from the estimated thermochemical equivalency. Completeness of reaction was verified by use of an analytical gas chromatograph with a capillary column and flame ionization detector on the spent calorimeter fluid.

Standards used in this work were 1-hexene,[14] $\Delta H_h = -126{\cdot}4 \pm 0{\cdot}8$ kJ mol^{-1}, and the unsubstituted styrene itself, $\Delta H_h = -117{\cdot}2 \pm 1{\cdot}7$ kJ mol^{-1}. After the values for styrene had been established using 1-hexene as the thermochemical standard, and cross-checked with results using electrical calibration,[15] styrene was preferred as the thermochemical standard for the rest of the unknowns. It was found that there was some degradation of the thermogram (i.e. reduction of the rate of heat produced) for 1-hexene, possibly owing to a differential adsorption strength of the phenyl group on the catalyst or its support (5% Pd on C).[16] Using styrene as the thermochemical standard gave more reproducible results than did 1-hexene, although there were no inconsistencies that exceeded the stated experimental uncertainty. (Error limits in our hydrogenation enthalpies are 95% confidence limits derived from seven injections of an unknown alternating with seven injections of a standard.)

RESULTS AND DISCUSSION

Dimethylamides

The results of the combustion experiments carried out with *N,N*-dimethylpivalamide, *N,N*-dimethyl-1-adamantylcarboxamide and *N,N*-dimethylbenzamide are given in Table 2, wherein the symbols used and the data are treated as in Ref. 17.

The specific energies of combustion of the three dimethylamides are referred to the final temperature of the experiments. The uncertainties in Table 2 are twice the final overall standard deviations of the mean and were estimated as outlined by Olofsson.[18] The values for the standard molar enthalpies of formation of H_2O(lq) and CO_2(g) at $T = 298{\cdot}15$ K,

Table 2. Results of combustion experiments

Compound	Parameter	Resultant values				
N,N-Dimethyl-*tert*-butylcarboxamide (lq)	m' (compound)/g	0·70639	0·68271	0·72384	0·76556	0·68357
	m'' (polyethene)/g	0·07580	0·07588	0·07457	0·07978	0·07453
	$\Delta t_c/\mathrm{K} = (t_f - t_i + \Delta t_{corr})/\mathrm{K}$	1·99496	1·93648	2·03459	2·15404	1·93355
	ε (calor.) $(-\Delta t_c)$/kJ	−28·4654	−27·6311	−29·0309	−30·7353	−27·5893
	ε (cont.) $(-\Delta t_c)$/kJ	−0·0338	−0·0326	−0·0346	−0·0370	−0·0325
	ΔU_{ign}/kJ	0·0477	0·0458	0·0472	0·0482	0·0479
	$\Delta U_{dec}(\mathrm{HNO_3})$/kJ	0·0479	0·0479	0·0482	0·0514	0·0479
	ΔU (corr. to std. states)/kJ	0·0090	0·0087	0·0092	0·0099	0·0087
	$-m'' \Delta_c u^0$ (polyethene)/kJ	3·5148	3·5185	3·4578	3·6994	3·4559
	$\Delta_c u^0$ (compound)/(kJ g^{-1}	−35·2210	−35·2166	−35·2331	−35·2206	−35·1997
	$\langle \Delta_c u^0$ (298·15 K)$\rangle$/(kJ g^{-1}	−35·2182 ± 0·0054				
N,N-Dimethyl-1-adamantylcarboxamide (cr)	m' (compound)/g	0·63938	0·75209	0·75927	0·75777	0·75847
	$\Delta t_c/\mathrm{K} = (t_f - t_i + \Delta t_{corr})/\mathrm{K}$	1·67398	1·96790	1·98678	1·98345	1·98480
	ε (calor.) $(-\Delta t_c)$/kJ	−23·8854	−28·0793	−28·3487	−28·3013	−28·3205
	ε (cont.) $(-\Delta t_c)$/kJ	−0·02265	−0·0321	−0·0323	−0·0324	
	ΔU_{ign}/kJ	0·0472	0·0481	0·0468	0·0476	0·0464
	$\Delta U_{dec}(\mathrm{HNO_3})$/kJ	0·0352	0·0406	0·0412	0·0415	0·0412
	ΔU (corr. to std. states)/kJ	0·0096	0·0115	0·0117	0·0116	0·0116
	$\Delta_c u^0$ (compound)/(kJ g^{-1}	−37·2547	−37·2445	−37·2482	−37·2579	−37·2509
	$\langle \Delta_c u^0$ (298·15 K)$\rangle$/(kJ g^{-1}	−37·2512 ± 0·0024				
N,N-Dimetylbenzamide (cr)	m' (compound)/g	0·85887	0·85725	0·85928	0·85659	0·85822
	$\Delta t_c/\mathrm{K} = (t_f - t_i + \Delta t_{corr})/\mathrm{K}$	1·99564	1·99152	1·99768	1·99123	1·99414
	ε (calor.) $(-\Delta t_c)$/kJ	−28·4743	−28·4155	−28·5034	−28·4109	−28·4525
	ε (cont.) $(-\Delta t_c)$/kJ	−0·0330	−0·03306	−0·0330	−0·0329	−0·0329
	ΔU_{ign}/kJ	0·0507	0·0479	0·0487	0·0486	0·0470
	$\Delta U_{dec}(\mathrm{HNO_3})$/kJ	0·0460	0·0460	0·0460	0·0460	0·0454
	$-\Delta U$ (corr. to std. states)/kJ	0·0151	0·0151	0·0151	0·0151	0·0151
	$\Delta_c u^0$ (compound)/(kJ g^{-1}	−33·0614	−33·0586	−33·0819	−33·0778	−33·0660
	$\langle \Delta_c u^0$ (298·15 K)$\rangle$/(kJ g^{-1}	−33·0691 ± 0·0046				

−285·830 ± 0·042 and −393·51 ± 0·13 kJ mol^{-1}, respectively, were taken from the recommendations of CODATA.[19]

The results of the Knudsen effusion experiments with *N,N*-dimethyl-1-adamantylcarboxamide and *N,N*-dimethylbenzamide are summarized in Table 3, which presents the values of temperature, time and mass of sublimed substance.

The vapor pressures were calculated, following our earlier studies,[10b] and least-squares fitted to the standard equation $\log(p/P_a) = A - B/T$. A and B were found to be (15·34 ± 0·04 and −5060·0 ± 13·5 K^{-1}, respectively, for *N,N*-dimethyl-1-adamantylcarboxamide and 15·46 ± 0·05 and −4686·1 ± 14·5 K^{-1}, respectively, for *N,N*-dimethylbenzamide. The enthalpies of sublimation at the mean temperature of the

Table 3. Vapor pressures

Compound	T/K	t/s	Δm/mg	p/Pa	$10^2\delta p/p$	T/K	t/s	Δm/mg	p/Pa	$10^2\delta p/p$
N,N-Dimethyl-1-adamantylcarboxamide	303·02	18360	1·94	0·0441	+0·400	314·90	15300	6·76	0·188	+0·340
	306·02	27900	4·26	0·0642	+0·260	317·93	19080	11·81	0·265	−0·592
	309·10	24600	5·45	0·0936	+0·0245	322·66	24780	26·39	0·460	+0·837
	312·15	18240	5·79	0·135	−0·181					
N,N-Dimethylbenzamide	288·83	20580	3·78	0·172	+0·671	299·69	11880	8·22	0·659	−0·383
	291·28	14760	3·67	0·234	+0·0294	302·25	11220	10·62	0·905	+0·847
	293·55	16020	5·31	0·312	+0·152	304·58	11700	14·41	1·18	+0·0667
	269·12	15300	6·90	0·427	−0·370					

experimental measurements were 96·9 ± 0·3 kJ mol^{-1} at 312·84 K and 489·7 ± 0·34 kJ mol^{-1} at 296·71 K, respectively. Following our earlier procedure,[20] the enthalpies of sublimation were corrected to 298·15 K by determining the $C^0_{p,m}$(cr) values by DSC and the $C^0_{p,m}$(g) values were calculated using the group-contribution scheme of Rihani and Doraiswamy.[21]

The standard molar energies and enthalpies of combustion for each compound in its condensed state at 298·15 K, the standard molar enthalpy of vaporization or sublimation and the standard molar enthalpies of formation for gaseous dimethylamides and the standard molar enthalpy of vaporization or sublimation are given in Table 4; we note the accidental near equality of the gaseous enthalpies of formation of the *N*,*N*-dimethyl derivatives of pivalamide and 1-adamantylcarboxamide.

Although our experimental result for crystalline *N*,*N*-dimethylbenzamide, (−175·7 ± 2·2 kJ mol^{-1}), is enigmatically and disconcertingly far from that obtained in a recent combustion calorimetric study[22a] (−153·9 ± 1·0 kJ mol^{-1}), it lies comfortably within the error bars from a recent literature enthalpy of reaction study[22b](−171·4 ± 5·9 kJ mol^{-1}). For the gas-phase species, Ref. 22a fails to give an enthalpy of formation for the gas-phase species while our result, −86·0 ± 2·2 kJ mol^{-1}, and that suggested in Ref. 22b,. −83·2 ± 8·6 kJ mol^{-1}, are concordant.

Styrenes

A theoretical check of the hydrogenation enthalpies was carried out by taking the difference in enthalpies of formation of the various styrenes and their hydrogenated product, calculated using the molecular mechanics package MM392 (which was bought from Technical Utilization). The results of experiment and computational theory are consistent within the error bars of the former, as documented in Table 5.

Enthalpies of hydrogenation of the various styrenes measured in dilute hydrocarbon solution are comparable to those in the gas phase.[2,13,23] If we take as given the values for the enthalpies of formation of gaseous alkylbenzenes, then the enthalpies of formation of the aromatic alkenes styrene, α-methylstyrene, *trans*-β-methylstyrene and β,β-dimethylstyrene may be calculated from the experimentally measured enthalpies of hydrogenation.

Starting with gaseous styrene itself, we deduce an enthalpy of formation of 147·9 ± 2·0 kJ mol^{-1}, in precise agreement with the value of 147·9 ± 1·5 kJ mol^{-1} found in the most thorough archive of the enthalpies of formation of organic compounds.[24] For α-methylstyrene, our value is 115·3 ± 2·34 kJ mol^{-1}. Surprisingly, this archive[24] gives the enthalpy of formation only for the liquid, 70·5 ± 1·2 kJ mol^{-1}. Making use of one of the simplest methods for estimating the enthalpy of vaporization of arbitrary hydrocarbons[25] (at 298 K, making use of solely the number of non-quaternary and quaternary carbons), we predict a phase-change enthalpy of 45·1 ± 1·0 kJ mol^{-1} and the desired gas-phase enthalpy of formation of 115·3 ± 1·5 kJ mol^{-1}, in precise agreement with our experiment.[26] Interestingly, from two other thermochemical archives[27] and a conference proceedings,[28] we may retrieve the desired gas-phase value as 113 kJ mol^{-1}, but none documents the origin of this corroborative number.

Still less has been reported about the thermochemistry of *trans*-β-methylstyrene. We derive a gas phase enthalpy of formation of 113·8 ± 1·5 kJ mol^{-1}. Only one of these archives (Ref. 27b) presents a value at all, namely 117 kJ mol^{-1}, the value also derivable from Refs 28. Recent base-catalyzed equilibration studies[29] show this species to be 23·3 ± 0·5 kJ mol^{-1} more stable than its isomer allylbenzene. Accepting the equality of gas- and (non-polar) liquid-phase hydrogenation enthalpies,[2,23] the enthalpy of formation of gas-phase allylbenzene is ascertained[30] to be 134·3 ± 1·1 kJ mol^{-1}. From this analysis, we would therefore conclude that the enthalpy of formation of *trans*-β-methylstyrene is 111·0 ± 1·2 kJ mol^{-1}. A value of 112 ± 2 kJ mol^{-1} is hereby suggested. The α- and β-methylation of styrene results in hydrocarbons with very nearly identical enthalpies of formation. Lack of commercial availability of adequately pure *cis*-β-methylstyrene precluded our determination of its enthalpy of hydrogenation. However, the above equilibration study[29] shows this alkene to be (11·0 ± 0·3) kJ mol^{-1} less stable than its *trans*-isomer, in good agreement with 9·1 kJ mol^{-1} found from molecular mechanics. As such, we deduce an enthalpy of formation of gaseous *cis*-β-methylstyrene of 123·0 ± 1·3 kJ mol^{-1}.

Finally, for β,β-dimethylstyrene we know of no literature enthalpy of formation for any phase. Our value for the gas phase is 86·0 ± 2·1 kJ mol^{-1}.

Table 4. Standard molar energies of combustion and enthalpies of combustion, formation and phase change at 298·15 K

Compound	$\Delta_c U^\circ_m$/kJ mol^{-1}	$\Delta_c H^\circ_m$/kJ mol^{-1}	$\Delta_f H^\circ_m$/kJ mol^{-1}	$\Delta_{vap} H^\circ_m$/kJ mol^{-1}	$\Delta_{sub} H^\circ_m$/kJ mol^{-1}	$\Delta_f H^\circ_m$(g)/kJ mol^{-1}
N,*N*-Dimethyl-*tert*-butylcarboxamide (lq)	−4550·3 ± 1·9	−4557·1 ± 1·9	−341·2 ± 2·1	55·1 ± 0·4		−286·1 ± 2·1
N,*N*-Dimethyl-1-adamantylcarboxamide (cr)	−7722·7 ± 2·1	−7733·2 ± 2·1	−383·6 ± 2·7		97·5 ± ·3	−286·1 ± 2·7
N,*N*-Dimethylbenzamide (cr)	−4933·7 ± 1·8	−4938·0 ± 1·8	−175·7 ± 2·2		89·7 ± 0·3	−86·0 ± 2·2

Table 5. Enthalpies of hydrogenation of styrene, α-methylstyrene, the β-methylstyrenes and β,β-dimethylstyrene

			$\Delta_{H2}H^{\circ}_{m}(g)$/kJ mol^{-1}	
Compound	Purity/mol%		Experimental	MM392[a]
Styrene	>99		−117·2 ± 2·1[b]	−115·7
			−117·2 ± 0·8[b]	
		Mean:	−117·2 ± 1·7	
			−118·0 ± 0·4[c]	
			−118·8 ± 0·4[c]	
		Mean:	−118·4 ± 0·4	
α-Methylstyrene	>99		−111·7 ± 1·3[b]	−110·6
			−111·7 ± 1·7[d]	
			−110·0 ± 2·9[b]	
		Mean:	−111·3 ± 2·1	
trans-β-Methylstyrene	99		−105·9 ± 2·1[b]	−107·5
			−105·4 ± 0·8[d]	
			−106·3 ± 1·2[b]	
		Mean:	−105·9 ± 1·3	
cis-β-Methylstyrene			—[e]	−116.6
β, β-Dimethylstyrene	99		−107·5 ± 1·7[d]	−107·2
			−107·5 ± 1·7[d]	
		Mean:	−107·5 ± 1·7	

[a] Hydrogenation enthalpies derived from molecular mechanics calculations are obtained as the difference of the calculated enthalpies of formation of the styrene and the corresponding saturated species.
[b] This work, 1-hexene thermochemical standard.
[c] From Ref. 15, electrical calibration.
[d] This work, styrene thermochemical standard.
[e] This isomer is not commercially available.

Thermochemical comparisons of amides, methyl ketones and related alkenes

Accompanying an earlier combustion study on pivalamide and 1-adamantylcarboxamide,[31] it was shown that the formal reaction

$$CH_3CONH_2(g) + RCOCH_3 \rightarrow (CH_3)_2CO(g) + RCONH_2(g) \quad (1)$$

is essentially thermoneutral for $R = C_2H_5$, *n*- and *i*-C_3H_7, *t*-C_4H_9 and 1-$C_{10}H_{15}$. This suggests that the strain energies and hence strain effects in the series $RCONH_2$ and $RCOCH_3$ are similar, as befits their isoelectronic and isosteric nature. Interestingly, on combining the enthalpy of sublimation[32a] and the remeasured and re-evaluated[32b] enthalpy of formation of solid benzamide (and archival values for everything else), we find that the reaction with $R = C_6H_5$ is endothermic by 7·3 ± 2·4 kJ mol^{-1}. The phenyl group is different from the other R groups because it can conjugate with the carbonyl group. As such, by being 'cross-conjugated,' benzamide has a reduced resonance and thus decreased thermodynamic stabilization from the sum of those of the 'component' amide and benzoyl moieties.

Let us consider formal reaction that compares amides with α-methylalkenes:

$$CH_3CONH_2(g) + RC(CH_3){=}CH_2 \rightarrow (CH_3)_2C{=}CH_2(g) + RCONH_2(g) \quad (2)$$

Using data taken solely from the archival source[24] for both $R = C_2H_5$ species in reaction (2), we find this reaction to be exothermic by 1·7 ± 1·75 kJ mol^{-1}. For $R = n\text{-}C_3H_7$, 2-methyl-1-pentene, we can either use the archival[24] enthalpy of formation found by combustion and vaporization from Ref. 23, −59·4 ± 1·3 kJ mol^{-1}, or the value of −58·7 ± 1·1 kJ mol^{-1} derived from measurement of its enthalpy of hydrogenation.[33] The two values are equal within experimental error. We choose the value from the latter, hydrogenation, approach because (a) hydrogenation calorimetry is preferable to combustion calorimetry for hydrocarbons C_6 or larger where a methodological 'competition' exists[34] and (b) in the absence of enthalpy of combustion experiments, we have only hydrogenation derived enthalpies of formation for many of the remaining alkenes in the current study. Reaction (2) for $R = n\text{-}C_3H_7$ is found to be endothermic by 0·7 ± 2·6 kJ mol^{-1}.

Within the error bars, the enthalpies of reaction (2) for R = C_2H_5 and *n*-C_3H_7 are equal to each other and are consistent with the assumption of thermoneutrality. We are not surprised: why should the results for ethyl and *n*-propyl differ?

We now turn to more complicated, and more sterically demanding, R groups. For R = *i*-C_3H_7, we have the same choice to make for the source of the enthalpy of the desired alkene 2,3-dimethyl-1-butene, −62·6 ± 1·3 kJ mol^{-1} (taken from Ref. 24) and −64·2 ± 1·2 kJ mol^{-1} (derived from Ref. 33, see above). Choosing the latter value because of our preference for recent hydrogenation calorimetric experiments, we find reaction (2) to be endothermic by 1·4 ± 2·0 kJ mol^{-1}. This reaction remains essentially thermoneutral. For R = *t*-C_4H_9, the two choices of the enthalpy of formation of gaseous 2,3,3-trimethyl-1-butene are different: combustion calorimetry gives −85·5 ± 1·4 kJ mol^{-1} while hydrogenation calorimetry (with alkene data from Ref. 35) gives −90·2 ± 1·4 kJ mol^{-1}. With our earlier measured value of the enthalpy of formation of pivalamide,[31] 313·1 ± 1·4 kJ mol^{-1}, and the hydrogenation-derived enthalpy of formation for the alkene, we find an exothermicity of 1·5 ± 2·3 kJ mol^{-1}. So far, reaction (2) has been seen to be essentially thermoneutral. This suggests that α-methyl alkenes are good 'mimics' of amides, much as methyl ketones were shown to be above. [We know of no thermochemical data for 1-(isopropenyl)adamantane, or its hydrogenation product, with which to attempt and understanding of 1-adamantanylcarboxamide.]

From our earlier analysis, we may expect a lack of thermoneutrality for reaction (2) R = C_6H_5. We find an endothermicity of 5·7 ± 2·9 kJ mol^{-1}, in accord with our expectation and understanding. We are encouraged.

Our next comparison removes the α-methyl group from the alkene for use in the equation

$$CH_3CONH_2(g) + RCH{=}CH_2 \rightarrow CH_3CH{=}CH_2(g) + RCONH_2(g) \quad (3)$$

For R = C_2H_5, *n*- and *i*-C_3H_7 (taking all data from Ref. 24), we find this reaction to be exothermic by 0·2 ± 1·6, endothermic by 0·4 ± 1·8 and endothermic by 3·3 ± 1·7 kJ mol^{-1}, respectively. For R = *t*-C_4H_9 (with alkene data from Ref. 33), the endothermicity has grown to 5·5 ± 2·1 kJ mol^{-1}. In that the strain resulting from the NH_2 of the amide and the CH_2 of the alkene are expected to be comparable, we would expect additional strain arising from repulsion of the oxygen in the amide with the R group relative to the olefinic hydrogen. As such, with R = C_6H_5 (with alkene data from the current study), the endothermicity is now increased to 10·0 ± 2·6 kJ mol^{-1}, a conceptually derived composite of 'mere' steric repulsion-derived instability and loss of conjugation-derived stabilization.

Thermochemical comparisons of *N*,*N*-dimethylamides with alkenes

Our preferred archive, Ref. 24, gives us only the liquid-phase enthalpy of formation of dimethylacetamide with which to compare our results on *N*,*N*-dimethylpivalamide, *N*,*N*-dimethyl-1-adamantylcarboxamide and *N*,*N*-dimethylbenzamide. It would appear that no enthalpy of formation data for gas-phase dimethylamides have been reported. However, modifying the criteria for data selection allows us to ameliorate this situation. To begin with, we use the recently reported[36] enthalpy of vaporization of dimethylacetamide.

A direct way of examining the energetics of *N*,*N*-dimethylamides is thus to consider the energetics of the formal reaction

$$CH_3CON(CH_3)_2(g) + RCONH_2(g) \rightarrow CH_3CONH_2(g) + RCON(CH_3)_2(g) \quad (4)$$

The enthalpies of formation of the gas-phase dimethylamides with R = C_2H_5 and *n*-C_3H_7 appear in an otherwise unpublished conference report,[37] −250·2 ± 1·0 and −270·9 ± 1·4 kJ mol^{-1}, respectively, from which we derive exothermicities of 1·5 ± 2·1 and 51·9 ± 2·4 kJ mol^{-1}, respectively. For the R = *i*-C_3H_7 species, we found irreproducible (although seemingly complete) combustion for only two of our 20 calorimetric runs. We have therefore ignored any discussion involving *N*,*N*-dimethylisobutyramide. (For the curious reader, these complete but irreproducible findings for *N*,*N*-dimethylisobutyramide are an energy of combustion of −2268·3 ± 6·7 J g^{-1} an enthalpy of combustion of −3885·4 kJ mol^{-1} and −336·3 and −281·8 kJ mol^{-1} for liquid and gaseous species, respectively.) For R = *t*-C_4H_9, using the gas-phase enthalpy of formation of pivalamide from Ref. 26 and the value for its dimethyl derivative from Table 3 here, we find an endothermicity of 1·.8 ± 3·0 kJ mol^{-1} while relatedly, for R = 1-adamantyl, we find an endothermicity of 22·7 ± 4·1 kJ mol^{-1}. It is undeniable that *N*,*N*-dimethylpivalamide and *N*,*N*-dimethyl-1-admantylcarboxamide are strained. For R = C_6H_5, using the enthalpy of formation of benzamide from Ref. 32 and of its *N*,*N*-dimethyl derivative from Table 3 here we find an endothermicity of 26·1 ± 3·2 kJ mol^{-1} for equation (4). It appears that *N*,*N*-dimethylbenzamide is also significantly strained.

To understand further the *N*,*N*-dimethylamides, comparisons analogous to those for the parent amides may be suggested. For example, paralleling equation (1) (and recalling our much earlier use of 3-methylbutanone as a model for studying amides and their resonance energy[3,38]), reaction (5) follows:

$$CH_3CON(CH_3)_2(g) + RCOCH(CH_3)_2(g) \rightarrow CH_3COCH(CH_3)_2(g) + RCON(CH_3)_2(g) \quad (5)$$

However, the desired enthalpy of formation thermochemical data for the isopropyl ketones are generally absent.

Likewise, equation (2) may be adapted to yield the equation

$$\mathrm{CH_3CON(CH_3)_2(g) + RC(CH_3){=\!=}C(CH_3)_2 \rightarrow (CH_3)_2C{=\!=}C(CH_3)_2(g) + RCON(CH_3)_2(g)} \qquad (6)$$

The use of this equation is likewise thwarted because enthalpy of formation data for tetrasubstituted alkenes are generally absent. As a class, trisubstituted alkenes are thermochemically better characterized. As such, consider equation (7), designed to parallel equation (3) with its omitted methyl group:

$$\mathrm{CH_3CON(CH_3)_2(g) + RCH{=\!=}C(CH_3)_2(g) \rightarrow CH_3CH{=\!=}C(CH_3)_2(g) + RCON(CH_3)_2(g)} \qquad (7)$$

For $R = C_2H_5$ n-C_3H_7 and *t*-C_4H_9 with input alkene enthalpy of formation data from Refs 33, 13a and 24, respectively we find equation (7) to be exothermic by 0·7 ± 2·4, endothermic by 1·2 ± 2·6 and endothermic by 5·1 ± 3·8 kJ $\mathrm{mol^{-1}}$, respectively. For *N*,*N*-dimethylbenzamide, using the experimental enthalpies of formation of this species and of β,β-dimethylstyrene from the current study , an endothermicity of 14·3 ± 3·2 kJ $\mathrm{mol^{-1}}$ is found. We find that the exo-/endothermicity of reaction (7) for *N*,*N*-dimethylamides is essentially the same as that for equation (3) for the parent amides. Equivalently, trisubstituted alkenes of the generic structure $\mathrm{RCH{=\!=}C(CH_3)_2}$ are good mimics for dimethylamides (see Table 6).

Some thoughts on monomethylamides and disubstituted alkenes

From the above we may deduce that the steric repulsion of the R group and the methyl *cis* to it contributes comparably to the strain in both the dimethylamide and trisubstituted alkenes It would be helpful if there were enthalpies of formation of separately isolable 'isomeric' (*Z*)- and (*E*)-monomethylamides to compare with the real, separable, isomeric disubstituted alkenes $\mathrm{RCH{=\!=}CHCH_3}$. In their absence, we may nonetheless look at the difference quantity

$$\delta(\mathrm{R}) = \{\Delta H_f^\circ(\mathrm{g, RCONH_2}) - \Delta H_f^\circ[\mathrm{g, RCON(CH_3)_2}]\} - \{\Delta H_f^\circ[\mathrm{g}, (E)\text{-}\mathrm{RCH{=\!=}CHCH_3}] - \Delta H_f^\circ[\mathrm{g}, (Z)\text{-}\mathrm{RCH{=\!=}CHCH_3}]\} \qquad (8)$$

This quantity may be conceptually simplified by recalling that the (*E*)- and (*Z*)-alkenes hydrogenate to the same product, and so, where needed (an where it can be done), we may cast the second bracket in terms of differences of hydrogenation enthalpies, i.e.

$$\delta(\mathrm{R}) = \{\Delta H_f^\circ(\mathrm{g, RCONH_2}) - \Delta H_f^\circ[\mathrm{g, RCON(CH_3)_2}]\} - \{\Delta H_{\mathrm{H2}}[\mathrm{g}, (Z)\text{-}\mathrm{RCH{=\!=}CHCH_3}] - \Delta H_{\mathrm{H2}}[\mathrm{g}, (E)\text{-}\mathrm{RCH{=\!=}CHCH_3}]\} \qquad (9)$$

Table 6. Enthalpy of formation of gaseous amides and related alkenes and the enthalpy of reactions (2) and (7) that interrelated them

	$\Delta_f H_m^\circ(g)/\mathrm{kJ\ mol^{-1}}$				$\Delta_r H_m^\circ(g)/\mathrm{kJ\ mol^{-1}}$	
R	$\mathrm{RCONH_2}$	$\mathrm{RC(CH_3){=\!=}CH_2}$	$\mathrm{RCON(CH_3)_2}$	$\mathrm{RCH{=\!=}C(CH_3)_2}$	Equation (2)	Equation (7)
Ch_3	-238.3 ± 0.8^{a}	-16.9 ± 0.9^{a}	-228.1 ± 1.5^{b}	-41.8 ± 1.1^{a}	0	0
C_2H_5	-258.9 ± 0.6^{a}	-35.3 ± 1.0^{a}	-250.2 ± 1.0^{c}	-63.2 ± 1.5^{d}	-2.2 ± 1.6	-0.7 ± 2.6
n-C_3H_7	-279.2 ± 0.9^{a}	-59.4 ± 1.3^{a}	-270.9 ± 1.4^{c}	-87.8 ± 1.4^{e}	1.6 ± 1.9	3.2 ± 2.7
i-C_3H_7	-282.6 ± 0.9^{a}	-62.6 ± 1.3^{a}			1.4 ± 1.9	—
t-C_4H_9	-313.1 ± 1.4^{f}	-90.2 ± 1.4^{g}	-286.1 ± 2.1^{h}	-104.9 ± 2.1^{a}	-1.5 ± 2.3	5.1 ± 3.5
1-$C_{10}H_{15}$	-319.0 ± 2.5^{f}		-286.1 ± 2.7^{h}		—	—
C_6H_5	-101.9 ± 1.5^{f}	113.8 ± 2.1^{g}	-86.0 ± 2.2^{g}	86.1 ± 2.1^{h}	5.7 ± 2.8	14.0 ± 3.6

[a] See Ref. 23.

[b] Enthalpy of formation found by summing that of the condensed phase from Ref. 23 with the enthalpy of vaporization from Ref. 32.

[c] See Ref. 33.

[d] Enthalpy of formation found by summing the enthalpy of hydrogenation (see Ref. 29) with the enthalpy of formation of corresponding alkane from Ref. 23.

[e] Enthalpy of formation found by summing the enthalpy of hydrogenation (see Ref. 12a) with the enthalpy of formation of corresponding alkane from Ref. 23.

[f] See Ref. 26.

[g] Enthalpy of formation found by summing the enthalpy of hydrogenation (see Ref. 31) with the enthalpy of formation of corresponding alkane from Ref. 23.

[h] Results from measurements of enthalpies of combustion and sublimation described in this paper.

[i] Derived by summing enthalpy of formation of solid amide from Ref. 28 and enthalpy of sublimation from Ref. 27.

[j] Enthalpy of formation found by summing the enthalpy of hydrogenation from this work with the enthalpy of formation of the corresponding alkylbenzene from Ref. 23.

In addition, this quantity may be conceptually simplified by realizing that the (*E*) and (*Z*)-alkenes may be equilibrated, and so, where needed (and where it can be done), we may cast the second bracket in terms of equilibration enthalpies, i.e.

$$\begin{aligned}\delta(\mathrm{R}) = \{&\Delta H^\circ_\mathrm{f}(\mathrm{g}, \mathrm{RCONH_2}) - \Delta H^\circ_\mathrm{f}[\mathrm{g}, \mathrm{RCON(CH_3)_2}]\} \\ &-\{\Delta H_\mathrm{r}[\mathrm{g}, (Z)\text{-}\mathrm{RCH{=\!=}CHCH_3}] \\ &\rightarrow [\mathrm{g}, (E)\text{-}\mathrm{RCH{=\!=}CHCH_3}]\}\end{aligned} \qquad (10)$$

For $R = CH_3$ and C_2H_5 (with alkene thermochemical data from Ref. 24) we find $\delta = -5{\cdot}9 \pm 2{\cdot}2$ and $-4{\cdot}4 \pm 2{\cdot}3$ kJ mol^{-1}, for $R = n\text{-}C_3H_7$ and $t\text{-}C_4H_9$ (with alkene hydrogenation data from Refs 33 and 36, respectively) $\delta = -2{\cdot}8 \pm 2{\cdot}2$ and $-16{\cdot}7 \pm 3{\cdot}3$ kJ mol^{-1} and for $R = C_6H_5$ (with alkene equilibration data from Ref. 29) $\delta = -4{\cdot}9 \pm 2{\cdot}7$ kJ mol^{-1}.

The reader may be disquieted by the fact that we have not employed isodesmic reasoning in the above strain energy analysis. The following isodesmic reaction may be written:

$$\begin{aligned}&\mathrm{RCONH_2} + (Z)\text{-}\mathrm{RCH{=\!=}CHCH_3} + \\ &\quad (E)\text{-}\mathrm{CH_3CH{=\!=}CHCH_3} + \mathrm{CH_3CON(CH_3)_2} \rightarrow \\ &\mathrm{RCON(CH_3)_2} + (E)\text{-}\mathrm{RCH{=\!=}CHCH_3} + \\ &\quad (Z)\text{-}\mathrm{CH_3CH{=\!=}CHCH_3} + \mathrm{RCONH_2}\end{aligned} \qquad (11)$$

Indeed, the strain energy of the dimethylamide $RCON(CH_3)_2$ may be defined as the endothermicity of this reaction, which in turn may be algebraically shown to equal the difference of $\delta(CH_3)$ and $\delta(R)$.

Within this definition, this difference vanishes (within error bars) for $R = C_2H_5$, $n\text{-}C_3H_7$ and C_6H_5 but is $10{\cdot}8 \pm 4{\cdot}3$ kJ mol^{-1} for $R = t\text{-}C_4H_9$. We therefore conclude that the dimethylamide methyl group that is *Z* to the R group fails to contribute meaningfully to the strain found in *N,N*-dimethylbenzamide and the other dimethylamides, except for *N,N*-dimethylpivalamide (and presumably *N,N*-dimethyl-1-adamantylcarboxamide), where both methyls contribute significantly to the strain. More precisely, it is expected in the disubstituted alkenes, the $R \ldots CH_3$ repulsion can be decreased by changing the internal $=\!=C(H)CH_3$ angles, i.e. relaxing the geometry. Equivalently, we recognize the greater strain in the trisubstituted alkenes as the two groups on the disubstituted side cannot escape each other. We recognize this as an example of 'buttressing', as earlier calorimetrically documented for polymethylated derivatives of phenanthrene[39] and benz[*a*]anthracene,[39] and even of benzene itself.[40]

CONCLUSION

Measurement of the enthalpies of combustion of amides, $RCONH_2$, and their *N,N*-dimethyl derivatives have allowed us to investigate strain energy effects arising from steric repulsion of the R group and the methyl situated *cis* to it. Measurements of the enthalpies of hydrogenation of variously methylated styrenes have allowed us to investigate strain effects in aromatic alkenes. From these and literature findings, we have compared the enthalpies of formation of amides and the corresponding alkenes and find that trisubstituted alkenes of the generic structure $RCH{=\!=}C(CH_3)_2$ are good thermochemical mimics for dimethylamides.

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APPENDIX

Adamantylalkenes

We have not mentioned 1-vinyladamantane or any of its methyl derivatives, which should belong in a discussion of adamantylcarboxamide and its *N*,*N*-dimethyl derivative. We obtained a sample of (E)-1-adamantylpropene from Professor Dennis P. Curran and his student Michael Palovich, synthesized by the procedure given in

Ref. 41, for which we are grateful. Our first two hydrogenation runs gave enthalpies of $17{\cdot}5 \pm 0{\cdot}8$ and $77{\cdot}0 \pm 2{\cdot}5$ kJ mol^{-1}. These results, although internally consistent, are *ca* 25 kJ mol^{-1} disparate from those of other alkenes and our preliminary molecular mechanical findings. We therefore consider it best to defer any discussion of (*E*)-1-adamantylpropene and, by inference, of any other admantylalkene.