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Structural effects on the thermochemical properties of carbonyl compounds

II. Enthalpies of combustion, vapour pressures and enthalpies of sublimation, and standard enthalpies of formation in the gaseous phase, of 1-adamantyl methyl ketone and of 1,1′-diadamantyl ketone

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The energies of combustion of 1-adamantyl methyl ketone, and 1,1′-diadamantyl ketone have been determined using a static bomb calorimeter. The vapour pressures have been measured over a temperature range of about 17 K by the Knudsen-effusion technique. From the experimental results the following quantities for the two compounds, at $T = 298.15$ K, have been derived:

Compound	$\Delta_f H^\circ_m(\text{cr})/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{sub}} H^\circ_m/\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f H^\circ_m(\text{g})/\text{kJ}\cdot\text{mol}^{-1}$
1-Adamantyl methyl ketone	-382.5 ± 3.1	84.2 ± 0.6	-298.3 ± 3.2
1,1′-Diadamantyl ketone	-476.8 ± 4.9	109.0 ± 1.8	-367.8 ± 5.2

Structural effects on $\Delta_f H^\circ_m(\text{g})$ for these and other ketones have been discussed.

1. Introduction

We are presently involved in a systematic study of structural effects on the gas-phase proton affinities "PA"s$^{(1, 2)}$ {*i.e.* the standard enthalpy changes for the reaction in the

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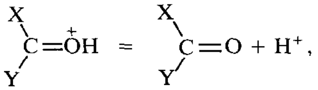
gas-phase}:



$$\mathrm{XYC{=}\overset{+}{O}H} = \mathrm{XYC{=}O} + \mathrm{H^+}, \qquad (1)$$

of carbonyl compounds XCOY. It is known(3,4) that the 1-adamantyl group ($1\text{-}C_{10}H_{15}$) is an extremely efficient charge-stabilizing substituent in the gas-phase, and this has led us to measure the PAs of several adamantyl ketones.(5) It is hoped that the determination of the enthalpies of formation of some of these compounds will facilitate the understanding of structural effects on the energetics of reaction (1).

In this work, we report a study of thermochemical properties of 1-adamantyl methyl ketone and of 1,1′-diadamantyl ketone. Purities, heat capacities, and phase transitions over the whole working-temperature range, were determined by d.s.c. Vapour pressures were measured over a 17 K interval by the Knudsen-effusion method. The energies of combustion were determined by combustion calorimetry. From the above results the standard molar enthalpies of sublimation and formation, in the crystalline and gaseous states, at the temperature 298.15 K were derived for the two compounds.

2. Experimental

1-Adamantyl methyl ketone was supplied by Aldrich-Chemie and purified by crystallization from aqueous ethanol. 1,1′-Diadamantyl ketone was prepared in excellent yield by Wieringa's method.(6) 1-Cyanoadamantane was refluxed with excess of dispersed sodium in hexane for 7 h, leading to the corresponding 1,1′-diadamantyl ketimine (90 per cent). Complete hydrolysis of this compound was achieved in nearly quantitative yield by means of a 40 h reflux with $5\,\mathrm{mol \cdot dm^{-3}}$ HCl(aq). Pure samples of 1,1′-diadamantyl ketone were obtained by crystallization from methanol. Infrared (KBr): $\tilde{\nu}(\mathrm{CO}) = 1660\,\mathrm{cm^{-1}}$. ^{1}H n.m.r. in $\mathrm{CDCl_3}$: $\delta = 2.00$ (18H); $\delta = 1.71$ (2H); unresolved multiplets. ^{13}C n.m.r. in $\mathrm{CDCl_3}$: $\delta = 217.11$ (CO); $\delta = 49.21$, $\delta = 39.27$, $\delta = 36.67$, $\delta = 28.38$ (1-Ad). Control of purity, assessed by d.s.c. by the fractional-fusion technique,(7) indicated that the mole fraction of impurities in each compound was <0.001. The samples were studied by d.s.c. over the whole working-temperature range and no phase transition was observed.

The combustion experiments were performed with a static bomb calorimeter. Apparatus and procedure have been described in references 8 to 10. The energies of combustion of the compounds were determined by burning the solid samples in pellet form in oxygen inside the bomb, with 1 cm^3 of water added to the bomb. Due to the relatively high vapour pressure of the 1-adamantyl methyl ketone, the pelleted compound was burnt enclosed in polyethene bags. The pellets of 1,1′-diadamantyl ketone were burnt also enclosed in polyethene bags, to initiate and ensure complete combustion. 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

TABLE 1. Physical properties at the temperature 298.15 K. Values in parentheses were estimated

Compound	$\frac{M}{\text{g}\cdot\text{mol}^{-1}}$	$\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}$	$\frac{(\partial u/\partial p)_T}{\text{J}\cdot\text{kPa}^{-1}\cdot\text{g}^{-1}}$	$\frac{c_p}{\text{J}\cdot\text{K}^{-1}\cdot\text{g}^{-1}}$
Polyethene	13.558	0.918	(0.00023)	2.0
1-Adamantyl methyl ketone	178.2736	1.18	(0.00006)	1.22
1,1′-Diadamantyl ketone	298.4674	1.13	(0.00006)	1.19

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 $-(26434 \pm 3)\ \text{J}\cdot\text{g}^{-1}$ under certificate conditions. Two values of the energy equivalent of the calorimeter were used in computing the combustion experiments: $\varepsilon(\text{calor}) = (14.2687 \pm 0.0004)\ \text{kJ}\cdot\text{K}^{-1}$, and $\varepsilon(\text{calor}) = (14.2685 \pm 0.0004)\ \text{kJ}\cdot\text{K}^{-1}$, for 1-adamantyl methyl ketone and 1,1′-diadamantyl ketone, respectively. The specific energy of combustion and empirical formula of polyethene are $-(46371 \pm 4)\ \text{J}\cdot\text{g}^{-1}$ and $C_{0.961}H_{2.000}$.(11) The corrections for nitric-acid formation were based on $-59.7\ \text{kJ}\cdot\text{mol}^{-1}$ for the molar energy of formation of $0.1\ \text{mol}\cdot\text{dm}^{-3}$ HNO_3(aq) from N_2, O_2, and H_2O(l). For the correction of weighings in air to masses, conversion of the energy of the actual bomb process to that of the isothermal process, and correction to standard states, we have used the values of density ρ, specific heat capacity c_p, and $(\partial u/\partial p)_T$, respectively, given in table 1. The densities were measured in our laboratory. Heat capacities were determined by d.s.c. Corrections to standard states were made according to the procedure given by Hubbard *et al.*(12)† The molar masses of the elements were those recommended by IUPAC in 1979.

The vapour pressures were measured by the Knudsen-effusion method, using the technique and procedure described previously.(13, 14) The apparatus consisted, essentially, of a stainless-steel sublimation chamber immersed in a jacket and connected to a high-vacuum system ($1 \cdot 10^{-4}$ Pa). The temperature of the jacket was maintained constant to within ±0.005 K for each vapour-pressure experiment, and was measured with a calibrated platinum resistance thermometer. The enthalpies of sublimation were computed from relations between pressure and temperature. The details of the two effusion orifices employed in the sublimation experiments carried out with the two compounds are: orifice area: $(0.799 \pm 0.003) \cdot 10^{-3}\ \text{cm}^2$, and Clausing coefficient: $W_a = (0.958 \pm 0.009)$ for 1-adamantyl methyl ketone; orifice area: $(6.69 \pm 0.01) \cdot 10^{-3}\ \text{cm}^2$, and Clausing coefficient: $W_a = (0.986 \pm 0.003)$ for 1,1′-diadamantyl ketone.

3. Results and discussion

The results of the combustion experiments carried out with 1-adamantyl methyl ketone and 1,1′-diadamantyl ketone are given in table 2. The symbols in this table

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† Throughout this paper the standard pressure p° was taken as 101.325 kPa.

TABLE 2. Results of combustion experiments

			1-Adamantyl methyl ketone		
m'(compound)/g	0.63538	0.63840	0.63524	0.63391	0.63531
m''(polyethene)/g	0.08079	0.08135	0.07094	0.06984	0.06979
$\Delta t_c/\mathrm{K} = (t_f - t_i + \Delta t_{corr})/\mathrm{K}$	1.98839	1.99896	1.95703	1.94907	1.95324
ε(calor)$(-\Delta t_c)$/kJ	−28.3718	−28.5226	−27.9242	−27.8107	−27.8702
ε(cont.)$(-\Delta t_c)$/kJ	−0.0324	−0.0326	−0.0318	−0.0316	−0.0317
ΔU_{ign}/kJ	0.0484	0.0489	0.0485	0.0482	0.0462
$\Delta U_{dec}(HNO_3)$/kJ	0.0059	0.0056	0.0056	0.0058	0.0044
ΔU(corr. to std. states)/kJ	0.0116	0.0117	0.0114	0.0114	0.0114
$-m''\Delta_c u^\circ$(polyethene)/kJ	3.7462	3.7722	3.2895	3.2385	3.2362
$\Delta_c u^\circ$(compound)/(kJ $\cdot$ g^{-1})	−38.7045	−38.7169	−38.7271	−38.7098	−38.7272
$\langle\Delta_c u^\circ(298.15\ \mathrm{K})\rangle$/(kJ $\cdot$ g^{-1})			−38.7171 ± 0.0046		
			1,1′-Diadamantyl ketone		
m'(compound)/g	0.59028	0.60866	0.60525	0.60713	0.60873
m''(polyethene)/g	0.07087	0.07134	0.07103	0.08172	0.07453
$\Delta t_c/\mathrm{K} = (t_f - t_i + \Delta t_{corr})/\mathrm{K}$	1.90401	1.95707	1.94615	1.98613	1.96781
ε(calor)$(-\Delta t_c)$/kJ	−27.1673	−27.9245	−27.7686	−28.3391	−28.0776
ε(cont.)$(-\Delta t_c)$/kJ	−0.0307	−0.0317	−0.0315	−0.0323	−0.0319
ΔU_{ign}/kJ	0.0474	0.0487	0.0472	0.0470	0.0486
$\Delta U_{dec}(HNO_3)$/kJ	0.0011	0.0020	0.0014	0.0012	0.0015
ΔU(corr. to std. states)/kJ	0.0110	0.0114	0.0113	0.0115	0.0115
$-m''\Delta_c u^\circ$(polyethene)/kJ	3.2862	3.3080	3.2937	3.7893	3.4559
$\Delta_c u^\circ$(compound)/(kJ $\cdot$ g^{-1})	−40.4083	−40.3937	−40.3908	−40.3905	−40.3989
$\langle\Delta_c u^\circ(298.15\ \mathrm{K})\rangle$/(kJ $\cdot$ g^{-1})			−40.3964 ± 0.0033		

have the same meanings as in reference 15, and the experimental values have also been derived as in reference 15. The specific energies of combustion of the two ketones are referred to the final temperature of the experiments. Table 3 gives the standard molar energies and enthalpies of combustion and the standard molar enthalpies of formation for the two compounds in the crystalline state at the temperature 298.15 K. The uncertainties in this table are twice the final overall standard deviations of the mean and were estimated as outlined by Olofsson.(16) The values for the standard molar enthalpies of formation of H_2O(l) and CO_2(g) at 298.15 K: $-(285.830 \pm 0.042)\ \mathrm{kJ \cdot mol^{-1}}$ and $-(393.51 \pm 0.13)\ \mathrm{kJ \cdot mol^{-1}}$, respectively, were taken from reference 17.

The results of our Knudsen-effusion experiments with the two compounds are summarized in table 4, which collects values of temperature, time, and mass of

TABLE 3. Standard molar energies of combustion and enthalpies of combustion and formation at 298.15 K ($p^\circ = 101.325$ kPa)

Compound (cr)	$\dfrac{\Delta_c U^\circ_m}{\mathrm{kJ \cdot mol^{-1}}}$	$\dfrac{\Delta_c H^\circ_m}{\mathrm{kJ \cdot mol^{-1}}}$	$\dfrac{\Delta_f H^\circ_m}{\mathrm{kJ \cdot mol^{-1}}}$
1-Adamantyl methyl ketone	−6902.2 ± 2.6	−6912.1 ± 2.6	−382.5 ± 3.1
1,1′-Diadamantyl ketone	−12057.0 ± 4.0	−12074.4 ± 4.0	−476.8 ± 4.9

TABLE 4. Vapour pressures

T/K	t/s	Δm/mg	p/Pa	$10^2 \cdot \delta p/p$	T/K	t/s	Δm/mg	p/Pa	$10^2 \cdot \delta p/p$
				1-Adamantyl methyl ketone					
286.56	20220	2.19	0.411	+1.99	298.78	24420	10.71	1.70	−0.746
288.94	21600	3.03	0.533	−1.17	301.71	17040	10.44	2.38	−0.0535
292.90	24360	5.48	0.862	+0.542	304.53	14100	11.88	3.29	+1.22
295.67	23460	7.29	1.19	−0.723					
				1,1′-Diadamantyl ketone					
361.95	19740	3.57	0.0690	+0.462	371.81	20220	8.76	0.167	−1.40
365.04	14760	3.43	0.0888	−3.07	375.29	20700	12.34	0.231	+0.306
368.37	17520	5.78	0.127	+2.17	378.79	15660	12.55	0.312	+0.0322

sublimed substance. The vapour pressures were calculated by means of the equation:

$$p = (\Delta m / W_a a t)(2\pi R T / M)^{1/2}. \qquad (2)$$

The symbols in this equation have the same meanings as in reference 14. The highest percentage error for the vapour pressure in table 4 is 0.5, computed as the sum of the estimated errors of all quantities in equation (2).

An equation of the type:

$$\lg(p/\mathrm{Pa}) = -B(T/\mathrm{K})^{-1} + A, \qquad (3)$$

was fitted to the results of table 4 by the least-squares method. The values $10^2 \cdot \delta p/p$ are the fractional deviations of the experimental vapour pressures from those computed using equation (3). The coefficients A and B of the equations corresponding to 1-adamantyl methyl ketone and 1,1′-diadamantyl ketone, are given in table 5. The enthalpies of sublimation of the compounds, corresponding to the mean temperature Θ of its experimental range, have been calculated from the corresponding B values and are also collected in table 5. The uncertainties assigned to the values of $\Delta_{\mathrm{sub}} H_{\mathrm{m}}$ are based on the standard deviations of B values.

The standard molar enthalpies of formation for both crystalline and gaseous phases, and the standard molar enthalpy of sublimation for each of the two compounds are given in table 6. The values for the enthalpies of sublimation at $T = 298.15$ K have been computed using the same equation as in reference 18. The $C^\circ_{p,\mathrm{m}}(\mathrm{cr})$ values have been determined in our laboratory by d.s.c., and $C^\circ_{p,\mathrm{m}}(\mathrm{g})$ values were calculated using the group-contribution scheme of Rihani and Doraiswamy.(19)

TABLE 5. Molar enthalpies of sublimation

Compound	Θ/K	A	B	$\dfrac{\Delta_{\mathrm{sub}} H_{\mathrm{m}}(\Theta)}{\mathrm{kJ \cdot mol^{-1}}}$
1-Adamantyl methyl ketone	295.55	14.97 ± 0.10	4402.9 ± 29.9	84.3 ± 0.6
1,1′-Diadamantyl ketone	370.37	13.62 ± 0.23	5350.3 ± 85.7	102.4 ± 1.6

TABLE 6. Standard molar enthalpies at the temperature 298.15 K

Compound	$\Delta_f H^\circ_m(\text{cr})$ / $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_{\text{sub}} H^\circ_m$ / $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f H^\circ_m(\text{g})$ / $\text{kJ}\cdot\text{mol}^{-1}$
1-Adamantyl methyl ketone	-382.5 ± 3.1	84.2 ± 0.6	-298.3 ± 3.2
1,1′-Diadamantyl ketone	-476.8 ± 4.9	109.0 ± 1.8	-367.8 ± 5.2

TABLE 7. Experimental values of $\Delta_f H^\circ_m(\text{g})$ for selected ketones RCOR′

R	R′	$\Delta_f H^\circ_m(\text{g})$ / $\text{kJ}\cdot\text{mol}^{-1}$
CH_3	CH_3	-217.3 ± 0.7 (20)
CH_3	$t\text{-}C_4H_9$	-290.7 ± 0.9 (21)
CH_3	$1\text{-}C_{10}H_{15}$	-298.3 ± 3.2 [a]
$t\text{-}C_4H_9$	$t\text{-}C_4H_9$	-345.8 ± 1.2 (22)
$1\text{-}C_{10}H_{15}$	$1\text{-}C_{10}H_{15}$	-367.8 ± 5.2 [a]

[a] This work.

No vapour pressures or combustion enthalpies of 1-adamantyl methyl ketone or of 1,1′-diadamantyl ketone have been found in the literature, for comparison with our results. Standard enthalpies of formation determined by other methods have not been found in the literature.

Consider the reactions:

$$2CH_3CO(t\text{-}C_4H_9)(g) = (CH_3)_2CO(g) + (t\text{-}C_4H_9)_2CO(g), \tag{4}$$

$$2CH_3CO(1\text{-}C_{10}H_{15})(g) = (CH_3)_2CO(g) + (1\text{-}C_{10}H_{15})_2CO(g). \tag{5}$$

Using standard molar enthalpies of formation from references 20 to 22, and this work, as summarized in table 7 the corresponding enthalpy changes, respectively $(18.3 \pm 1.9)\ \text{kJ}\cdot\text{mol}^{-1}$ and $(11.5 \pm 6.9)\ \text{kJ}\cdot\text{mol}^{-1}$, are obtained. Although the experimental uncertainties are relatively large, it is clear that reaction (5) is less endothermal or (at the most) as endothermal as reaction (4). This implies that, notwithstanding the larger overall bulk of the adamantyl group, the 1,3 strain(20) in $(1\text{-}C_{10}H_{15})_2CO$ is not larger than in $(t\text{-}C_4H_9)_2CO$.

In the Taft and Topsom formalism(4, 5) the 1-adamantyl group has an appreciably larger polarizability than the *ter*-butyl group. In the "big four" series: CH_3, C_2H_5, $i\text{-}C_3H_7$, $t\text{-}C_4H_9$, both polarizability and steric hindrance increase simultaneously. The use of the 1-adamantyl group as a substituent might be a convenient way of breaking this trend.

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