Strain effects in phenyl substituted methanes. Geminal interactions between phenyl and alkoxycarbonyl substituent

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Abstract

The standard (p^0=0.1 MPa) molar enthalpies of formation $\Delta_f H_m^0(l)$ at the temperature T=298.15 K were measured using combustion calorimetry for ethyl-2-phenyl-acetate, methyl-2-phenyl-propionate, and ethyl-2-phenyl-propionate. The standard molar enthalpies of vaporization of $\Delta_l^g H_m^0$ of these compounds were obtained from the temperature function of the vapour pressure measured in a flow system. Noticeable destabilized interactions of phenyl and alkoxycarbonyl substituents were derived from the enthalpies of formation in the gas phase of the compound under investigation. These values provide a further improvement to the group-contribution methodology for estimation of the thermodynamic properties of organic compounds © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The quantitative relationship between structure and energetics of organic compounds have been of interest to us for a long time [1–5]. Whilst modern bond-energy schemes give excellent correlations between observed and calculated $\Delta_f H_m^0(g)$ values for mono-substituted alkanes, and for poly-substituted alkanes when the substituents are far apart, deviation may arise when substituents are adjacent to geminal C-atom. Stabilization may occur due to anomeric effect or π-electron delocalization, but destabilization can arise from dipole–dipole repulsion of geminal substituents. Recently, we have reported that the resulting interactions of two and three alkoxycarbonyl substituents

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ajacent to the central C-atom lead to a meaningful destabilization effects of 10–50 kJ mol^{-1} due to dipole–dipole repulsion among these geminal substituents [4]. The phenyl substituent provide the possibility of π-electron delocalization, but at the same time could give a rise for a dipole–dipole repulsion with any of electron-withdrawing groups (F, CN, CO$_2$R). However, the question remains what is the interaction energy between phenyl and alkoxycarbonyl (CO$_2$R) substituent geminal ajacent to the central C-atom. To solve this problem, the standard molar enthalpies of formation in gas phase of ethyl-2-phenyl-acetate, methyl-2-phenyl-propionate, and ethyl-2-phenyl-propionate (Fig. 1) were determined on the basis of calorimetrically measured energies of combustion and molar enthalpies of vaporization determined by a transpiration method. Strain enthalpies H_S of phenylalkanoates were derived from their standard molar
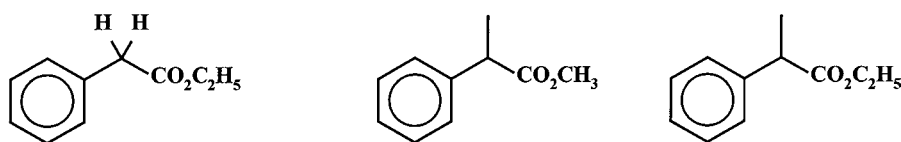
Fig. 1. Structures of investigated compounds: ethyl-2-phenyl-acetate, methyl-2-phenyl-propionate, ethyl-2-phenyl-propionate.

enthalpies of formation in the gaseous phase. The strain effects in terms of departure of enthalpies of formation from the group additivity rules were discussed.

2. Experimental

2.1. Materials

Ethyl-2-phenyl-acetate was purchased from Acros. Methyl-2-phenyl-propionate and ethyl-2-phenyl-propionate were synthesized via reaction of appropriate acyl chlorides with alcohols [6]. The structures of the compounds synthesized were established by n.m.r. spectroscopy. Liquid compounds were purified by repeated distillations using a spinning-band column at reduced pressure. The determination of purity was carried out by g.c. (sensitivity ≥0.01%). The purity of the samples for the combustion experiments is listed Table 1. To avoid traces of water in samples for the combustion experiments, the purified liquid samples were dried over molecular sieves and distilled once more before the combustions. Such a procedure provided colourless material, and the absence of water was verified by Karl Fischer titration.

2.2. Combustion calorimetry

For measurements of the enthalpies of combustion of phenylalkanoates an isoperibolic macrocalorimeter with a static bomb and a stirred water bath was used. The substances were placed in polyethylene capsules and were burned in oxygen at 3.04 MPa pressure. To ensure equilibrium in the final state, 0.78 g of water was added to the bomb. The detailed procedure has been described previously [7,8]. The combustion products were examined for carbon monoxide (Dräger tube) and unburnt carbon, but neither was detected. The energy of ignition was determined to be 1.46 J. The energy equivalent of the calorimeter ϵ_{calor} (see Tables 2 and 3) was determined with a standard reference sample of benzoic acid (sample SRM 39i, NIST). For the reduction of the data to standard conditions, conventional procedures [9] were used. The atomic weights used were those recommended by the IUPAC Commission [10,11]. The summary of auxiliary quantities for the combustion experiments and information necessary for reducing apparent mass to mass is given Table 1. The results for a typical combustion experiment on each compound are given Table 3. The individual values of the standard specific energy of combustion $\Delta_c u^0$ together with the mean

Table 1

Formula, purity, density $\rho_{(293\ K)}$, specific heat $c_{p(298.15\ K)}$, and expansion coefficient of the materials

	Formula	Purity (%)	$\rho_{(293\ K)}$ [a] (g cm^{-3})	$c_{p(298.15\ K)}$ [b] (J K^{-1} g^{-1})	$10^{-6}(\delta V_m/\delta T)_p$ [c] (dm^3 K^{-1})
Ethyl-2-phenyl-acetate	$C_{10}H_{12}O_2$	99.99	1.031	2.06	1.0
Methyl-2-phenyl-propionate	$C_{10}H_{12}O_2$	99.93	1.055	1.84	1.0
Ethyl-2-phenyl-propionate	$C_{11}H_{14}O_2$	99.93	0.999	2.01	1.0
Cotton [d]	$CH_{1.77}O_{0.89}$		1.500	1.67	0.1
Polyethylene [e]	$CH_{1.93}$		0.920	2.53	0.1

[a] Measured with pycnometer.
[b] From DSC-measurements.
[c] Estimted.
[d] $\Delta_c u^0$(cotton)=−(16945.2±4.2)J g^{-1}, where $\Delta_c u^0$ denotes standard specific energy of combustion.
[e] $\Delta_c u^0$ (polyethylene)=−(46361.0±3.1)J g^{-1}.

Table 2
Results of measurements of the vapour pressure p by the transpiration method

T (K) [a]	m (mg) [b]	$V(N_2)$ (dm^3) [c]	p (Pa) [d]
Ethyl-2-phenyl-acetate; $\ln(p/\text{Pa})=(27.88\pm0.17)-(7682\pm53)\cdot(T/\text{K})^{-1}$			
288.2	0.914	4.17	3.329
293.2	1.01	2.93	5.238
298.2	0.944	1.73	8.251
303.2	1.27	1.50	12.81
308.2	1.29	0.980	19.86
313.2	1.32	0.700	28.40
318.2	1.14	0.410	41.97
323.2	1.21	0.300	61.05
328.2	1.26	0.226	84.43
$\Delta_l^g H_m^0(308.2\,\text{K}) = (63.87 \pm 0.44)\text{kJ mol}^{-1}$; $\Delta_l^g H_m^0(298.15\,\text{K}) = (64.47 \pm 0.44)\text{kJ mol}^{-1}$			
Methyl-2-phenyl-propionate; $\ln(p/\text{Pa})=(27.20\pm0.27)-(7434\pm81)\cdot(T/\text{K})^{-1}$			
283.6	4.49	26.32	2.660
293.5	1.61	3.97	6.261
298.5	1.56	2.34	10.20
303.5	5.11	5.25	14.77
308.4	2.34	1.57	22.58
313.4	2.16	1.01	32.41
318.3	3.04	1.01	45.42
$\Delta_l^g H_m^0(300.9\,\text{K}) = (61.81 \pm 0.67)\text{kJ mol}^{-1}$; $\Delta_l^g H_m^0(298.15\,\text{K}) = (61.98 \pm 0.67)\text{kJ mol}^{-1}$			
Ethyl-2-phenyl-propionate; $\ln(p/\text{Pa})=(27.47\pm0.11)-(7599\pm33)\cdot(T/\text{K})^{-1}$			
293.4	2.16	6.34	4.767
298.3	2.08	3.95	7.340
303.6	2.14	2.67	11.16
308.4	1.92	1.57	17.04
313.7	2.96	1.60	25.76
318.7	3.91	1.45	37.47
323.7	2.52	0.653	53.56
328.6	2.89	0.525	76.54
$\Delta_l^g H_m^0(311.0\,\text{K}) = (63.18 \pm 0.27)\text{kJ mol}^{-1}$; $\Delta_l^g H_m^0(298.15\,\text{K}) = (63.95 \pm 0.27)\text{kJ mol}^{-1}$			

[a] Temperature of saturation, N_2 gas flow (0.26–0.52) cm^3 s^{-1}.
[b] Mass of transferred sample condensed at T=243 K.
[c] Volume of nitrogen used to transfer sample.
[d] Vapour pressure at temperature T of experiment; corrections were made for residual vapour pressure at T=243 K.

and its standard deviation, are given in Table 4. To derive $\Delta_f H_m^0(g)$ from $\Delta_c H_m^0$, the following molar enthalpies of formation were used [10]: for $H_2O(l)$: $-(285.83\pm0.04)$ kJ mol^{-1}, and for $CO_2(g)$: $-(393.51\pm0.13)$ kJ mol^{-1}. Table 5 lists the derived standard molar enthalpies of combustion, and standard molar enthalpies of formation in the condensed and gaseous states. The assigned standard deviations of the mean include the uncertainties from calibration, from the combustion energies of the auxiliary materials, and reaction products H_2O and CO_2.

2.3. Transpiration method

The enthalpies of vaporization of phenylalkanoates were determined with the method of transference in a saturated N_2-stream [12,13] using Clausius–Clapeyron equation. About 0.5 g of the sample was mixed with glass beads and placed in a thermostatted U-tube of length 20 cm and diameter 0.5 cm. At constant temperature (±0.1 K), a nitrogen stream was passed through the U-tube and the transported amount of material was collected in a cooled trap. The vapour

Table 3
Results of typical combustion experiments at 298.15 K [a]

	Ethyl-2-phenyl-acetate	Methyl-2-phenyl-propionate	Ethyl-2-phenyl-propionate
m(substance) (g) [b]	0.366896	0.583413	0.442730
m'(cotton) (g) [b]	0.001078	0.000807	0.001039
m''(polyethene) (g) [b]	0.506979	0.274024	0.274685
ΔT_c (K) [c]	1.40543	1.25159	1.09216
$(\epsilon_{calor})\cdot(-\Delta T_c)$ (J)	−35261.54	−31430.68	−27426.98
$(\epsilon_{cont})\cdot(-\Delta T_c)$ (J)	−20.29	−17.9	−15.07
ΔU_{corr} (J) [d]	15.50	15.34	12.13
$-m'\cdot\Delta_c u'$ (J)	18.26	13.67	17.60
$-m''\cdot\Delta_c u''$ (J)	23504.04	12704.00	12734.68
$\Delta_c u^0$(substance) (J g^{-1})	−32005.4	−32076.2	−33149.1

[a] For the definition of the symbols see [8]; T_h=298.15 K; V(bomb)=0.2664 dm^3; p^i(gas)=3.04 MPa; m^i(H$_2$O)=0.78 g; ΔU(ign)=1.46 J; m(Pt)=12.18 g.
[b] Masses obtained from apparent masses.
[c] $\Delta T_c = T^f - T^i + \Delta T_{corr}$; $(\epsilon_{cont})\cdot(-\Delta T_c) = (\epsilon^i_{cont})\cdot(T^i - 298.15\ K) + (\epsilon^f_{cont})\cdot(298.15\ K - T^f + \Delta T_{corr})$; ϵ_{calor}=(25089.5±1.2) J K^{-1} for ethyl-2-phenyl-acetate; and ϵ_{calor}=(25112.6±1.9) J K^{-1} for other compounds.
[d] ΔU_{corr}, the correction to standard state, is the sum of items 81–85, 87–90, 93 and 94 in [8].

Table 4
Values of specific energies of combustion $\Delta_c u^0$ at T=298.15 K (p^0=0.1 MPa); $\langle\Delta_c u^0\rangle$ denotes mean value

Ethyl-2-phenyl-acetate	Methyl-2-phenyl-propionate	Ethyl-2-phenyl-propionate
$-\Delta_c u^0$ (J g^{-1})		
32005.4	32076.2	33149.1
32020.9	32069.3	33158.2
32037.7	32073.4	33142.6
32039.3	32074.3	33138.5
32010.4	32082.6	33156.6
$\langle-\Delta_c u^0\rangle$ (J g^{-1})		
32022.7±6.9	32075.2±2.2	33149.0±3.8

pressure p was corrected for the residual vapour pressure at the condensation temperature. The latter was calculated from a linear correlation between ln(p) and T^{-1} obtained by iteration. The molar enthalpies of vaporization were calculated from the slope of the linear Clausius–Clapeyron correlation. The observed enthalpies of vaporization $\Delta_l^g H_m^0 (T)$ at the tempera-ture T obtained by this procedure are listed Table 2. Because of the deviations from T=298.15 K of the average temperatures of measurement by transpiration method, the observed values of the enthalpies of vaporization of phenylalkanoates (see Table 2) had to be corrected to this reference temperature. The corrections were estimated with the help of the

Table 5
Experimental results for phenylalkanoates at T=298.15 K

	$\Delta_c H_m^0$ [a] (kJ mol^{-1})	$\Delta_f H_m^0 (l)$ (kJ mol^{-1})	$\Delta_l^g H_m^0$ [b] (kJ mol^{-1})	$\Delta_f H_m^0 (g)$ (kJ mol^{-1})
Ethyl-2-phenyl-acetate	−5263.3±1.2	−386.8±2.5	64.47±0.44	−322.3±2.5
Methyl-2-phenyl-propionate	−5271.89±0.56	−378.18±1.4	61.98±0.67	−316.2±1.6
Ethyl-2-phenyl-propionate	−5914.45±0.84	−415.0±1.7	63.95±0.27	−351.01±1.7

[a] Calculated from the massic enthalpies of combustion in Table 4.
[b] From the measurements of vapour pressure at different temperatures from Table 2 using the Clausius–Clapeyron equation.

"Sidgwick correction":

$$\{\Delta_l^g H_m^0(\langle T \rangle) - \Delta_l^g H_m^0(298.15\,\text{K})\}/(\text{kJ}\,\text{mol}^{-1})$$
$$= -6 \times 10^{-2}\{(\langle T \rangle/\text{K}) - 298.15\},$$

following the recommendation of Chickos et al. [14]. With these corrections and the measured values of $\Delta_l^g H_m^0(T)$ from Table 2, the standard molar enthalpies at T=298.15 K were calculated (Tables 2 and 5).

3. Results and discussion

The thermochemical properties of methyl-2-phenyl-propionate and ethyl-2-phenyl-propionate were determined for the first time. The only previous determination of the standard molar enthalpy of combustion of ethyl-2-phenyl-acetate was made by Roth and Müller [15]. Their value $\Delta_c H_m^0 = -(5243.9 \pm 4.2)\,\text{kJ}\,\text{mol}^{-1}$ is in disagreement with ours $-(5263.3 \pm 1.2)\,\text{kJ}\,\text{mol}^{-1}$. The discrepancy could be attributed to the traces of water which are impossible to remove using only distillation.

3.1. Calculation of strain enthalpies H_s

Conventional strain-enthalpies were derived as the differences between the observed enthalpies of formation in the gaseous state and values calculated for strain-free structures by applying group additivity schemes with parameters taken from the literature [16,17]. The system of strain-free increments is based on the standard enthalpies of formation $\Delta_f H_m^0(g)$ of simple homologous ("strainless") molecules. Strain-free group additivity increments for hydrocarbons [17] and arenes [18] are well defined. Their advantage with respect to the classic Benson increments [16] is the possibility to determine strain enthalpies. All the increments necessary in this work are as follows [17,18]: $CH_3[C]=-42.05\,\text{kJ}\,\text{mol}^{-1}$; $CH_2[2C]=-21.46\,\text{kJ}\,\text{mol}^{-1}$; $CH[3C]=-9.04\,\text{kJ}\,\text{mol}^{-1}$; $C[4C]=-1.26\,\text{kJ}\,\text{mol}^{-1}$; $C_BH[2C_B]=13.72\,\text{kJ}\,\text{mol}^{-1}$; $C_B[C,2C_B]=23.51\,\text{kJ}\,\text{mol}^{-1}$; ($C_B$ represents the aromatic C atoms). Strain-free group additivity increments for ester [4]: $CH_3[CO_2]=-42.05\,\text{kJ}\,\text{mol}^{-1}$; $CH_2[CO_2,C]=-17.4\,\text{kJ}\,\text{mol}^{-1}$; $CH[CO_2,2C]=-7.4\,\text{kJ}\,\text{mol}^{-1}$; $CH_3[O]=-42.05\,\text{kJ}\,\text{mol}^{-1}$; $CH_2[O,C]=-33.8\,\text{kJ}\,\text{mol}^{-1}$. Using these group-additivity parameters given and the values of $\Delta_f H_m^0(g)$ of compounds (Table 5) derived in this research, the values of strain enthalpies $H_s = (\Delta_f H_m^0(g) - \sum \text{increments})$ of phenylalkanoates have been estimated. These resulting interactions are listed Table 6.

All studied phenylalkanoates have strain energy of 6–10 kJ mol^{-1} (see Table 6). The strain energy of iso-propylbenzene, H_s=5.03 kJ mol^{-1}, calculated from its enthalpy of formation $\Delta_f H_m^0(g) = 4.0 \pm 1.0\,\text{kJ}\,\text{mol}^{-1}$ [19] has been included in each molecule under investigation. This strain describes the intrinsic strain of the iso-propylbenzene due to sterical repulsions of methyl groups and benzene ring attached to the tertiary carbon atom. The comparison with this strain allowed the derivation of the strain effects of interactions of phenyl and alkoxycarbonyl substituents on the central C-atom directly. We calculated the differences between individual strains for each compound studied in this work and the strain of iso-propylbenzene (Table 6). These values were interpreted as the resulting interactions of phenyl and alkoxycarbonyl substituents adjacent to the central C-atom. The quantities of these interactions indicated (Table 6) the weak destabilization (about 5 kJ mol^{-1}) independent of the type of sub-

Table 6
Strain interactions of phenyl and alkoxycarbonyl substituent in phenylalkanoates at T=298.15 K (in kJ mol^{-1})

	$\Delta_f H_m^0(g)$ (exp)	$\Delta_f H_m^0(g)$ (calc) [a]	H_s [b]	H_s [c]	Δ [d]
Ethyl-2-phenyl-acetate	-322.3 ± 2.5	-328.2	6.0	–	6.0 ± 2.5
Methyl-2-phenyl-propionate	-316.2 ± 1.6	-326.4	10.2	5.0	5.2 ± 1.6
Ethyl-2-phenyl-propionate	-351.01 ± 1.7	-360.2	9.2	5.0	4.2 ± 1.7

[a] Calculated as the sum of strain-free increments (see text).
[b] Strain enthalpy of benzyl derivatives $H_s = \Delta_f H_m^0(g)(\text{exp}) - \Delta_f H_m^0(g)(\text{calc})$.
[c] Strain enthalpy of alkylbenzene H_s taken from [18].
[d] The sum of resulting interactions of phenyl substituent and ester group: $\Delta = H_s(\text{phenylalkanoate}) - H_s(\text{alkylbenzene})]$ (see text). The uncertainties of the interactions were suggested to be only equal to those of the experimental $\Delta_f H_m^0(g)$.

stitution of the central C-atom. Obviously, the observed geminal destabilization arise mainly from the repulsive forces between the phenyl and ester group by dipolar interactions. This amount of the geminal destabilization is substantially lower than in the malonic ester derivatives, where dipole–dipole repulsion between two alkoxycarbonyl groups exhibits geminal destabilization of 9–17 kJ mol^{-1} [4].

Acknowledgements

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