

Thermochemical investigation on α -methyl-styrene and parent phenyl substituted alkenes

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Abstract

The standard molar enthalpies of vaporization $\Delta_1^g H_m^0$ or sublimation $\Delta_{cr}^g H_m^0$ of α -methyl-styrene, 4-methoxy- α -methyl-styrene, 1,1-di-(4-methyl-phenyl)-ethene, allyl benzene, 1,2-dihydro-naphthalene, and 1,4-dihydro-naphthalene were obtained from the temperature function of the vapor pressure measured in a flow system. The standard ($p^0=0.1$ MPa) molar enthalpies of formation $\Delta_f H_m^0$ (l or cr) at $T=298.15$ K were measured using combustion calorimetry for α -methyl-styrene, 4-methoxy- α -methyl-styrene, and 1,1-di-(4-methyl-phenyl)-ethene. Molar enthalpies of fusion $\Delta_{cr}^l H_m^0$ of the solid compounds were measured by DSC. These experimental results together with the data available from the literature provided a coherent understanding of the energetics of phenyl-substituted species. The results of the study were also aimed at an improvement of the group-contribution methodology. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Enthalpy of combustion; Enthalpy of vaporization; Enthalpy of formation; Group-additivity correlation; Alkenes

1. Introduction

Owing to the many interesting aspects (delocalization of a π bond by resonance, steric strain, twist angle of the phenyl ring about the phenyl–vinyl bond) in the structures and energetics of phenyl-substituted alkenes (Fig. 1), a knowledge of their thermochemical properties was considered desirable. Surprisingly, the thermochemistry for these compounds is in disarray. A considerable number of investigations have been done on the α -methyl-styrene (Table 1) from both, experimental and theoretical [1] points of view. An easy ability of α -methyl-styrene to undergo polymerization seriously aggravates its purification and study, and has

thwarted all efforts to reliably determine the thermochemical properties (especially measurements of enthalpy of combustion, where the scatter of the results is 10–50 kJ mol⁻¹). Also, the only apparent proper value of $\Delta_f H_m^0(l) = 70.5 \pm 1.2$ kJ mol⁻¹ of α -methyl-styrene is not stainless, because it was measured on the sample containing 0.4 mass% of styrene as an impurity [2]. The ambiguous gas-phase value of $\Delta_f H_m^0(g) = 113$ kJ mol⁻¹ for α -methyl-styrene (Table 1) was retrieved without any reference from the thermochemical archive [3] and has allowed this property to be misused for a long time. The gaseous enthalpy of formation of α -methyl-styrene derived by indirect methods from the equilibrium study of aldol condensations: $\Delta_f H_m^0(g) = 118.3 \pm 1.4$ kJ mol⁻¹ [4] and the recent result from hydrogenation enthalpies: $\Delta_f H_m^0(g) = 115.3 \pm 2.3$ kJ mol⁻¹ [5], remain

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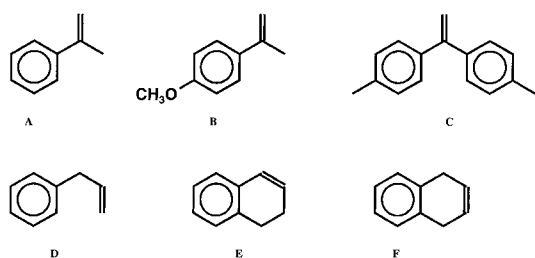


Fig. 1. Structures of molecules studied: α -methylstyrene (A), 4-methoxy- α -methylstyrene (B), 1,1-di-(4-methyl-phenyl)-ethene (C), allylbenzene (D), 1,2-dihydro-naphthalene (E), and 1,4-dihydro-naphthalene (F).

Table 1

Comparison of thermochemical properties of α -methylstyrene with earlier experimental values (in kJ mol^{-1}) at $T=298.15\text{ K}$

$-\Delta_c H_m^0$	$\Delta_f H_m^0(l)$	$\Delta_f^g H_m^0$	$\Delta_f H_m^0(g)$
5093.2 [20]			113.0 [3]
5041.2 \pm 1.1 [2]	70.5 \pm 1.2 [2]		118.3 \pm 1.4 [4]
5083.8 [21]			120.1 [1] ^a
		48.64 \pm 0.35 [22]	115.3 \pm 2.3 [5]
<i>This work</i>			
5040.8 \pm 0.8	70.07 \pm 0.82	48.92 \pm 0.27	118.99 \pm 0.86

^a Calculated with ERW force-field calculation using parameters developed in Ref. [7].

ambiguous, even though they are in agreement. The reliability of these values is somewhat shadowed by the inherent assumptions commonly used when handling such data. The MM3 force field calculation [6] predicts the gas-phase enthalpy of formation of $\Delta_f H_m^0(g) = 115.4\text{ kJ mol}^{-1}$. The ERW force-field calculation [7] developed especially for the olefins provides $\Delta_f H_m^0(g) = 120.1\text{ kJ mol}^{-1}$ [1] very close to the experiment. In view of the disappointing ambiguity of the experimental and theoretical data (refer Table 1), we have been encouraged to redetermine the enthalpy of combustion and enthalpy of vaporization for α -methylstyrene.

The substituent effects on the benzene ring have been of interest to us for a long time [8–10]. In this study, having established the thermochemical quantities for α -methylstyrene, it raises an interesting question, whether the charge distribution between double bond and phenyl ring corresponds to the introduction of an electron-donating methoxy group in 4-methoxy- α -methylstyrene?

The investigation of thermochemical properties of allylbenzene, 1,2-dihydro-naphthalene, and 1,4-dihydro-naphthalene (Fig. 1) allowed an investigation of the interactions of the benzene ring and the double bond, attached or separated from each other. The extent of strain in six-membered rings could be assessed from a comparison of this data set. The standard enthalpies of vaporization $\Delta_f^g H_m^0$ for allylbenzene, 1,2-dihydro-naphthalene, and 1,4-dihydro-naphthalene were measured in order to obtain $\Delta_f H_m^0(g)$ for those compounds from known data [11,12] for $\Delta_f H_m^0(l)$ and to involve experimental data for interpretation in the gaseous state.

The success of empirical additive schemes, such as Benson's tables [13,14], in calculating thermochemical properties of organic compounds suggests that most of the group-additive values applied by this procedure are reliable. Virtual, the experimental database to derive a plethora of increments, is not expansive enough in order to take into account the diversity of possible combinations of atoms. Thus, due to rigorous constraint, some gaps in the database have been filled with approximations. The reliability of such quantities is, however, questionable. The experimental results for α -methylstyrene (A), 1,1-di-(4-methyl-phenyl)-ethene (C), and allylbenzene (D), will serve for the improvement of the structural increments C_d [C_b , C], C_d [$2C_b$] and $-\text{CH}_2$ [C_b , C_d]. The quantities of these terms were only assessed [13] and proposed for redefining in the recent recalculation of the Benson's additive terms [14].

2. Experimental

All the compounds were purchased from Aldrich or Acros. The g.l.c. analyses on the purchased samples gave an average purity of 0.98 mass fraction in agreement with specifications. Liquid samples were washed with 5% NaOH, dried over CaCl_2 and purified by repeated distillation (in the presence of sodium-potassium alloy for final drying) under reduced pressure using spinning-band column. The solids were purified by repeated crystallization from petroleum ether or ethanol and, finally, sublimed at reduced pressure to remove any traces of the solvent. The degree of purity was determined by g.l.c. No impurities (mass fraction $>1 \times 10^{-4}$) could be detected in

Table 2

Results from typical combustion experiments at $T=298.15$ K ($p^0=0.1$ MPa)^a

	α -Methyl-styrene	4-Methoxy- α -methyl-styrene	1,1-di-(4-Methyl-phenyl)-ethene
m (substance)/g ^b	0.845000	0.399687	0.352201
m' (cotton)/g ^b	0.001088	0.000801	0.001080
m'' (auxiliary)/g ^b	0.276439 ^g	0.058716 ^h	0.070955 ^h
ΔT_c /K ^c	1.94345	0.70114	0.71309
$(\varepsilon_{\text{calor}})(-\Delta T_c)$ /J ^d	-48832.87	-17607.45	-17907.54
$(\varepsilon_{\text{cont}})(-\Delta T_c)$ /J ^e	-27.31	-8.96	-9.09
$\Delta U_{\text{corr.}}$ /J ^f	24.80	8.15	8.28
$-m'\Delta_c u'/J$	18.43	13.57	18.30
$-m''\Delta_c u''/J$	12816.00	2701.16	3264.20
$\Delta_c u^0$ (substance)/(J g ⁻¹)	-42602.8	-37259.5	-41522.7

^a For the definition of the symbols see Ref. [18]; $T_h=298.15$ K; $V(\text{bomb})=0.2664$ dm³; $p^i(\text{gas})=3.04$ MPa; $m^i(\text{H}_2\text{O})=0.78$ g; $\Delta U(\text{ign})=1.46$ J; $m(\text{Pt})=12.18$ g.

^b Masses obtained from apparent masses.

^c $\Delta T_c=T^f-T^i+\Delta T_{\text{corr.}}$; $\varepsilon_{\text{calor}}=(25126.9\pm 1.9)$ J K⁻¹ for compound (A).

^d $\varepsilon_{\text{calor}}=(25112.6\pm 1.9)$ J K⁻¹ for compounds (B) and (C).

^e $(\varepsilon_{\text{cont}})(-\Delta T_c)=(\varepsilon_{\text{cont}}^i)(T^i-298.15\text{ K})+(\varepsilon_{\text{cont}}^f)(298.15\text{ K}-T^f+\Delta T_{\text{corr.}})$.

^f $\Delta U_{\text{corr.}}$, the correction to standard state is the sum of items 81 to 85, 87 to 90, 93, and 94 in Ref. [18].

^g Combustion in the polyethen container.

^h Combustion with addition of oil.

samples for thermochemical study. For solid compounds, mass fractions 0.9999 were additionally established by DSC measurements of the melting process [15]. The pure samples were stored cold in the dark, either at reduced pressure or in a nitrogen atmosphere.

We used the following equipment: g.l.c., Carlo Erba Fraktometer Vega Series GC 6000, Hewlett–Packard Integrator 3390A, N₂-flow 0.333 cm³ s⁻¹, SE-30 capillary column of length 25 m. Standard temperature program of the g.l.c. at 313 K for 5 min at a flow rate of 0.167 K s⁻¹ up to $T=523$ K. Specific heat capacities and enthalpy of fusion were determined with a Perkin–Elmer DSC-2C.

For measurements of the energies of combustion of phenyl-alkenes, an isoperibolic macrocalorimeter with a static bomb and a stirred water bath was used. Taking into account the ability of α -methyl-styrene for self-polymerization, for each combustion experiment only a freshly distilled sample was used. The liquid substances were placed in polythene capsules, and were then burned in oxygen at a pressure 3.04 MPa. The duration of the combustion experiment until ignition was <1 h. After that time, the remainder of sample was analyzed (g.l.c) for dimers and oligomers of α -methyl-styrene, but neither was detected. The

solid samples were pressed into pellets of mass ca. 400 mg, the completeness of the combustion was ensured by the addition of about 50 mg of oil to the pellet. The detailed procedure has been described previously [16,17]. The combustion products were examined for carbon monoxide (Dräger tube) and unburnt carbon, but neither was detected. The energy of ignition was determined at 1.46 J. The energy equivalent of the calorimeter $\varepsilon_{\text{calor}}$ (see Table 2) was determined with a standard reference sample of benzoic acid (sample SRM 39i, N.I.S.T.). For the reduction of the data to standard conditions, conventional procedures [18] were used. The atomic weights used were those recommended by the IUPAC Commission [19]. The densities of the commercially available liquid compounds were taken from the Aldrich catalog. The densities of the solid substances were determined by submerging tablets of the substances in water in a calibrated 10 cm³ pycnometer. The summary of auxiliary quantities for the combustion experiments and information necessary for reducing apparent mass to mass is given in Table 3.

The enthalpies of vaporization or sublimation of phenyl-alkenes were determined by the method of transference in a saturated N₂-stream [23,24] using

Table 3
Temperature T_{fus} , density $\rho(293\text{ K})$, specific heat capacity $c_p(298.15\text{ K})$, and coefficients of expansion $(\delta V_m/\delta T)_p$ of the materials

	$T_{\text{fus}}^{\text{a)}}$ K	$\rho(293\text{ K})^{\text{b)}}$ (g cm^{-3})	$c_p(298.15\text{ K})^{\text{a)}}$ ($\text{J K}^{-1}\text{ g}^{-1}$)	$10^{-6}(\delta V_m/\delta T)_p^{\text{c)}}$ ($\text{dm}^{-3}\text{ K}^{-1}$)
α -Methyl-styrene	—	0.909	1.38	1.0
4-Methoxy- α -methyl-styrene	309.2	1.064	1.26	0.1
1,1-di-(4-Methyl-phenyl)-ethene	334.1	1.105	1.37	0.1
Oil ^d	—	0.880	0.84	1.0
Cotton ^e	—	1.500	1.67	0.1
Polyethene ^f	—	0.920	2.53	0.1

^a From DSC measurements.

^b Measured with the pycnometer.

^c Estimated.

^d From nine combustion experiments $\Delta_c u^0(\text{CH}_{1.940}) = -(46003.6 \pm 4.0)\text{ J g}^{-1}$.

^e From ten combustion experiments $\Delta_c u^0(\text{CH}_{1.774}\text{O}_{0.887}) = -(16945.2 \pm 4.2)\text{ J g}^{-1}$.

^f From eleven combustion experiments $\Delta_c u^0(\text{CH}_{1.930}) = -(46361.0 \pm 3.1)\text{ J g}^{-1}$.

Clausius–Clapeyron equation. Almost 0.5 g of the sample was mixed with glass beads and placed in a thermostated U-tube of 20 cm length and 0.5 cm diameter. At constant temperature ($\pm 0.1\text{ K}$), a nitrogen stream was passed through the U-tube and the transported amount of material was collected in a cooled trap. The $0.28\text{--}0.56\text{ cm}^3\text{ s}^{-1}$ flow range of the nitrogen stream is optimal in order that the transporting gas may reach the saturation equilibrium at each temperature investigated. The amount of condensed substance was determined by g.l.c. analysis using an internal standard (hydrocarbons, $n\text{-C}_{11}\text{H}_{24}$ or $n\text{-C}_{13}\text{H}_{28}$). In order to avoid possible polymerization of the phenyl-alkenes during, and after, transpiration, the cold traps were washed with solution containing traces of 4-*tert*-butyl-catechol. The vapor pressure p at each saturation temperature was calculated from the amount of product collected within a definite time period with the help of the ideal gas equation. The measured value of the vapor pressure, p , at each temperature was independent of the gas flow in the broad range from 0.1 to $0.8\text{ cm}^3\text{ s}^{-1}$, which has proved the saturation of the transported gas with the compound. The vapor pressure p was corrected for the residual vapor 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 $\Delta_f^g H_m^0 = -R(d \ln p/dT^{-1})$. The observed enthalpies of vaporization $\Delta_f^g H_m^0(T)$ at the tempera-

ture T , obtained by this procedure, are listed in Table 4.

3. Results and discussion

The results for a typical combustion experiment on each compound are given in Table 2. The individual values of the standard specific energy of combustion $\Delta_c u^0$, together with the mean and its standard deviation, are given in Table 5. To derive $\Delta_f H_m^0(\text{g})$ from $\Delta_c H_m^0$, the following molar enthalpies of formation were used [19]: for $\text{H}_2\text{O}(\text{l})$ $-(285.83 \pm 0.04)\text{ kJ mol}^{-1}$, and for $\text{CO}_2(\text{g})$ $-(393.51 \pm 0.13)\text{ kJ mol}^{-1}$. Table 6 lists the derived standard molar enthalpies of combustion, and standard molar enthalpies of formation in the condensed and gaseous states. The given standard deviations of the mean include the uncertainties from calibration and the uncertainties from the combustion energies of the auxiliary materials.

Results from numerous studies of the enthalpy of combustion of α -methyl-styrene (A) are listed in Table 1. The result reported in [2] is in excellent agreement with our value. Other values for the enthalpy of combustion [20,21] are in very poor agreement with the latter. The purity of the samples from those investigations was generally claimed to be 99 mass%, but no other details for each individual compound was given, making these results of historical interest only.

The measurements of thermochemical properties of 4-methoxy- α -methyl-styrene (B) have been made for the first time.

Table 4
Results from measurements of the vapor pressure p with the transpiration method

T/K^a	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
<i>α-Methyl-styrene; $\ln p/Pa=25.52-5913.8(T/K)^{-1}$</i>							
273.7	6.32	2.922	48.69	298.3	8.97	0.631	301.7
278.4	7.19	2.194	72.11	303.3	9.52	0.489	411.9
283.3	6.97	1.436	105.2	308.3	8.47	0.316	566.0
288.3	8.06	1.152	150.2	313.5	5.67	0.157	761.0
293.4	8.24	0.820	214.2				
$\Delta_f^g H_m^0(293.6\text{ K})=49.17\pm 0.27\text{ kJ mol}^{-1}$; $\Delta_f^g H_m^0(298.15\text{ K})=48.92\pm 0.27\text{ kJ mol}^{-1}$							
<i>4-Methoxy-α-methyl-styrene; $\ln p/Pa=26.90-7292.1(T/K)^{-1}$</i>							
308.2	10.7	7.180	24.92	328.4	6.87	1.050	109.5
314.9	9.23	3.660	42.20	333.4	5.77	0.630	153.3
318.1	6.85	2.160	53.08	338.2	10.2	0.830	205.0
323.2	9.47	2.090	75.81	343.3	5.90	0.350	282.2
$\Delta_f^g H_m^0(325.7\text{ K})=60.63\pm 0.29\text{ kJ mol}^{-1}$; $\Delta_f^g H_m^0(298.15\text{ K})=62.13\pm 0.29\text{ kJ mol}^{-1}$							
<i>1,1-Di-(4-methyl-phenyl)-ethene; $\ln p/Pa=32.21-12063(T/K)^{-1}$</i>							
309.4	0.817	64.07	0.1517	323.4	1.75	24.40	0.8542
313.2	0.894	42.38	0.2509	326.8	1.42	14.21	1.187
314.7	0.907	37.66	0.2864	331.6	1.45	8.23	2.089
318.2	0.907	22.97	0.4695				
$\Delta_{cr}^g H_m^0(320.6\text{ K})=100.3\pm 1.4\text{ kJ mol}^{-1}$; $\Delta_{cr}^g H_m^0(298.15\text{ K})=101.0\pm 1.4\text{ kJ mol}^{-1}$							
<i>Allyl-benzene; $\ln p/Pa=24.92-5592.6(T/K)^{-1}$</i>							
273.8	3.80	0.990	87.30	298.2	6.04	0.270	476.3
278.5	4.29	0.765	124.5	303.1	6.24	0.211	627.6
283.3	4.59	0.571	175.4	308.2	6.07	0.149	861.1
288.1	5.05	0.450	242.1	313.4	5.01	0.091	1162.0
293.4	5.63	0.346	348.0				
$\Delta_f^g H_m^0(293.6\text{ K})=46.50\pm 0.16\text{ kJ mol}^{-1}$; $\Delta_f^g H_m^0(298.15\text{ K})=46.25\pm 0.16\text{ kJ mol}^{-1}$							
<i>1,2-Dihydro-naphthalene; $\ln p/Pa=24.86-6245.7(T/K)^{-1}$</i>							
274.4	1.20	2.979	8.116	300.2	1.85	0.607	58.65
278.3	1.08	1.822	11.78	303.5	1.69	0.437	74.25
283.3	1.53	1.822	16.47	308.5	2.04	0.376	103.7
288.2	1.73	1.402	23.93	313.5	2.26	0.318	136.0
293.3	1.66	0.897	35.67	318.5	2.66	0.260	195.0
296.3	1.69	0.737	44.04				
$\Delta_f^g H_m^0(296.4\text{ K})=51.93\pm 0.37\text{ kJ mol}^{-1}$; $\Delta_f^g H_m^0(298.15\text{ K})=51.93\pm 0.37\text{ kJ mol}^{-1}$							
<i>1,4-Dihydro-naphthalene; $\ln p/Pa=29.50-7696.2(T/K)^{-1}$</i>							
274.4	0.740	3.434	4.221	288.1	1.36	1.616	16.19
278.3	0.684	2.100	6.321	293.2	1.39	1.034	25.70
283.2	1.11	2.100	10.20	296.2	1.49	0.850	33.43
$\Delta_{cr}^g H_m^0(285.3\text{ K})=63.99\pm 0.16\text{ kJ mol}^{-1}$; $\Delta_{cr}^g H_m^0(298.15\text{ K})=63.58\pm 0.16\text{ kJ mol}^{-1}$							
<i>1,4-Dihydro-naphthalene; $\ln p/Pa=25.17-6400.9(T/K)^{-1}$</i>							
300.1	1.68	0.700	46.01	318.2	2.39	0.300	152.3
303.3	1.52	0.500	58.15	323.2	2.56	0.234	208.6
308.3	1.87	0.434	82.25	328.2	2.52	0.166	289.9
313.3	2.21	0.366	115.2	333.3	3.08	0.150	391.8
$\Delta_f^g H_m^0(316.7\text{ K})=53.22\pm 0.38\text{ kJ mol}^{-1}$; $\Delta_f^g H_m^0(298.15\text{ K})=54.23\pm 0.38\text{ kJ mol}^{-1}$							

^a Temperature of saturation, N_2 gas flow $0.26\text{--}0.52\text{ cm}^3\text{ s}^{-1}$.

^b Mass of transferred sample condensed at $T=243\text{ K}$.

^c Volume of nitrogen used to transfer sample.

^d Vapour pressure at temperature T of experiment; corrections were made for residual vapour pressure at $T=243\text{ K}$.

Table 5

Values of specific energies of combustion $-\Delta_{cu}^0$ (in J g^{-1}) at $T=298.15$ K as the results of all combustion experiments

α -methyl-styrene	4-methoxy- α -methyl-styrene	1,1-di-(4-methyl-phenyl)-ethene
42602.8	37259.5	41501.4
42579.1	37266.6	41522.7
42599.7	37267.1	41516.7
42614.6	37275.3	41514.1
42609.3	37277.3	41519.4
Mean value:		
42601.1 \pm 6.1	37269.2 \pm 3.2	41514.9 \pm 3.7

The only previous determination of the standard enthalpy of formation $\Delta_f H_m^0(\text{cr})$ of 1,1-di-(4-methyl-phenyl)-ethene (C) has been made by Coops et al. [25], using combustion calorimetry. Their value $\Delta_f H_m^0(\text{cr}) = (85.9 \pm 2.1) \text{ kJ mol}^{-1}$ is in very poor agreement with our value of $(74.9 \pm 1.0) \text{ kJ mol}^{-1}$. The sample for combustion was carefully recrystallized from alcohol by Coops et al. [25], but they did not determine the degree of purity of this compound. Therefore, their value $\Delta_f H_m^0(\text{cr})$ seems to be doubtful.

The resulting enthalpies of vaporization or sublimation are given in Table 4. Because of the deviations of the average temperatures of measurement by transpiration method from $T=298.15$ K, the observed values of the enthalpies of vaporization or sublimation (see Table 4) had to be corrected to this reference temperature. The corrections were estimated with the help of the following correlations:

$$\{\Delta_1^g H_m^0(\langle T \rangle) - \Delta_1^g H_m^0(298.15 \text{ K})\} / (\text{kJ mol}^{-1}) \\ = -5.44 \times 10^{-2} \{(\langle T \rangle / \text{K}) - 298.15\},$$

$$\{\Delta_{\text{cr}}^g H_m^0(\langle T \rangle) - \Delta_{\text{cr}}^g H_m^0(298.15 \text{ K})\} / (\text{kJ mol}^{-1}) \\ = -3.20 \times 10^{-2} \{(\langle T \rangle / \text{K}) - 298.15\},$$

according to the recommendation of Chickos et al. [26]. With these corrections, and the measured values of $\Delta_1^g H_m^0(T)$ and $\Delta_{\text{cr}}^g H_m^0$ from Table 4, the standard molar enthalpies at $T=298.15$ K were calculated (Tables 4 and 6).

Surprisingly, determination of the enthalpy of vaporization of α -methyl-styrene (A) has been made using ebulliometry only recently by Steele et al. [22]. Their value of $\Delta_1^g H_m^0$ is consistent with our work as can be seen by referring to Table 1. The measurement

of the enthalpy of vaporization of other compounds, B–F, was done for the first time. Here, some affirmative comparisons could be made to provide reliability of the measured values. Thus, it is logical to expect that the difference, 2.3 kJ mol^{-1} , between enthalpies of vaporization of 1,2-dihydro-naphthalene and 1,4-dihydro-naphthalene (Table 6) has to be the same as the difference, 1.88 kJ mol^{-1} , between enthalpy of vaporization of 1,2-cyclohexadiene $\Delta_1^g H_m^0 = 33.17 \pm 0.05 \text{ kJ mol}^{-1}$ [30] and 1,4-cyclohexadiene $\Delta_1^g H_m^0 = 35.05 \pm 0.04 \text{ kJ mol}^{-1}$ [30], because of the similar shape of these couples.

The values derived in this work for $\Delta_f H_m^0(\text{g})$ for α -methyl-styrene are highly consistent (Table 1) with the values obtained from equilibrium studies [4,5] and also with the theoretical value from ERW force field calculation [1]. The value of $\Delta_f H_m^0(\text{g})$, derived in this work, for allyl-benzene (Table 6) is in excellent agreement with the value of $(134.3 \pm 1.1) \text{ kJ mol}^{-1}$, obtained from hydrogenation enthalpies recently [5].

3.1. Estimation of the group-additivity contributions

The group-additivity scheme of Benson type [13,14] is widely used for the calculation of standard molar enthalpies of formation at 298 K. The structural increment $C_d [C_b, C] = 41.1 \text{ kJ mol}^{-1}$ was calculated from the experimental value $\Delta_f H_m^0(\text{g})$ for α -methyl-styrene with the help of other Benson's increments from recent compilation [14]. This increment is in excellent agreement with the values $C_d [C_b, C] = 41.0 \text{ kJ mol}^{-1}$ calculated from $\Delta_f H_m^0(\text{g}) = 281.2 \text{ kJ mol}^{-1}$ for 2,5-di-phenyl-hexadiene-1,5 [27], and the value $C_d [C_b, C] = 38.9 \text{ kJ mol}^{-1}$ calculated from $\Delta_f H_m^0(\text{g}) = 255.6 \text{ kJ mol}^{-1}$ for 2,6-di-phenyl-heptadiene-1,6 [27]. The average group-additivity value $C_d [C_b, C] = 40.3 \text{ kJ mol}^{-1}$ was calculated as the mean value from these three increments. From $\Delta_f H_m^0(\text{g})$ of 1,1-di-(4-methyl-phenyl)-ethene (C), the contribution $C_d [2C_b] = 28.1 \text{ kJ mol}^{-1}$ was calculated. This increment is within acceptable limits, with the value $C_d [2C_b] = 32.6 \text{ kJ mol}^{-1}$ calculated from $\Delta_f H_m^0(\text{g}) = (245.6 \pm 4.4) \text{ kJ mol}^{-1}$ for 1,1-di-phenyl-ethene [28]. The group-additivity value $C_d [C_b, C] = 30.4 \text{ kJ mol}^{-1}$ is the average of these two increments. From $\Delta_f H_m^0(\text{g})$ of allyl benzene, the contribution $\text{CH}_2[C_b, C_d] = -20.1 \text{ kJ mol}^{-1}$ was obtained. It is suggested that the quantities for these terms complete

Table 6
Thermochemical results at $T=298.15$ K ($p^0=0.1$ MPa) in kJ mol^{-1}

	State	$-\Delta_c H_m^0$ (l or cr) ^a	$\Delta_f H_m^0$ (l or cr)	$\Delta_l^g H_m^0$ ^b	$\Delta_{cr}^l H_m^0$ ^c	$\Delta_{cr}^g H_m^0$ ^b	$\Delta_f H_m^0$ (g)
α -methyl-styrene (A)	l	-5040.80 ± 0.82	70.07 ± 0.82	48.92 ± 0.27	—	—	118.99 ± 0.86
4-methoxy- α -methyl-styrene (B)	cr	-5529.7 ± 0.66	-120.34 ± 0.66	62.13 ± 0.29	19.07 ± 0.21	81.20 ± 0.36	-39.14 ± 0.75
1,1-di-(4-methyl-phenyl)-ethene (C)	cr	-8657.7 ± 1.0	74.9 ± 1.0	—	23.31 ± 0.21	101.0 ± 1.4	175.9 ± 1.7
allyl-benzene (D)	l	—	88.0 ± 1.2 [11,28]	46.25 ± 0.16	—	—	134.3 ± 1.2
1,2-dihydro-naphthalene (E)	l	—	71.5 ± 1.7 [12,28]	51.93 ± 0.37	—	—	123.4 ± 1.7
1,4-dihydro-naphthalene (F)	cr	—	84.2 ± 1.5 [12,28] ^d	54.23 ± 0.38 ^e	9.35 ± 0.41 ^f	63.58 ± 0.16	138.4 ± 1.6

^a Calculated from the specific energies of combustion in Table 5. ^b Calculated from the measurements of vapour pressure at different temperatures from Table 4 using the Clausius-Clapeyron equation.

^c From DSC measurements

^d Referred to the liquid state [12,28].

^e Measured above the melting temperature.

^f Estimated as the difference $\Delta_{cr}^g H_m^0 - \Delta_l^g H_m^0$ from this table; melting temperature was 298.1 K.

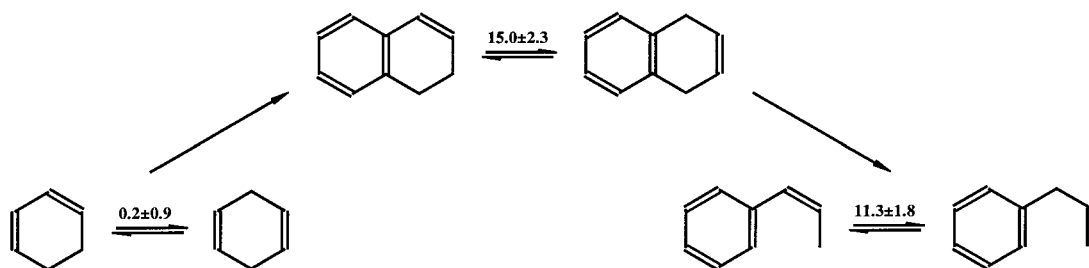


Fig. 2. Isomerisation enthalpies (in kJ mol^{-1}) of mutual interconversions of some selected alkenes.

the recent recalculation of the Benson's additive terms [14].

3.2. Calculation of interactions of substituents on the benzene ring

We define the strain of a molecule as the difference between the experimental standard enthalpy of formation $\Delta_f H_m^0$ and the calculated sum of increments of the Benson type [14] for a molecule. Using these group-additivity parameters [14] and the value of $\Delta_f H_m^0$ of 4-methoxy- α -methylstyrene (Table 6) derived in this research, the value of strain enthalpies $H_s \equiv (\Delta_f H_m^0(\text{g}) - \Sigma_{\text{increments}}) = -8.3 \text{ kJ mol}^{-1}$ for 4-methoxy- α -methylstyrene have been estimated. This quantity for substituents indicates the noticeable stabilization of the benzene ring, due to interaction of the electron-donating methoxy group with established charge distribution between the double bond and the phenyl ring.

From thermochemical results for allyl benzene, 1,2-dihydronaphthalene, and 1,4-dihydronaphthalene, the interactions of the benzene ring with the double bond, attached or separated from each other, could be derived (Fig. 2). In order to obtain the relative stabilities, the isomerization enthalpies of the following (Fig. 2) three reactions were calculated from the gas-phase enthalpies of formation of 1,2-cyclohexadiene ($\Delta_f H_m^0(\text{g}) = 104.58 \pm 0.63 \text{ kJ mol}^{-1}$) [30] and 1,4-cyclohexadiene ($\Delta_f H_m^0(\text{g}) = 104.75 \pm 0.59 \text{ kJ mol}^{-1}$) [30], 1,2-dihydronaphthalene and of 1,4-dihydronaphthalene (Table 6), and *cis*- β -methylstyrene ($\Delta_f H_m^0(\text{g}) = 123.0 \pm 1.3 \text{ kJ mol}^{-1}$) [5] and allyl benzene (Table 6). Surprisingly, from the first reaction, both the cyclohexadienes showed the same stability, according to their experimental enthalpies of formation. However, from the second reaction, it is evident

that the enthalpy of formation of 1,4-dihydronaphthalene, 15.0 kJ mol^{-1} , is less stable than that of its 1,2-isomer. The conjugation of the double bond with an aromatic ring in the 1,2-position is responsible for such a stabilization. Support for this observation could be also obtained from the results for the third reaction. There, it could be seen that *cis*- β -methylstyrene is about 11.3 kJ mol^{-1} , that is to say it is more stable than its positional isomer with the double bond separated from the benzene ring. The stabilizing effects of the latter reactions are significantly different though they are very close, because in case of the second reaction the important contribution could be expected from the strain of the six-membered unsaturated ring in dihydronaphthalene. The extent of these strains: $H_s = -2.5 \text{ kJ mol}^{-1}$ in 1,2-dihydronaphthalene and $H_s = 6.0 \text{ kJ mol}^{-1}$ for 1,4-dihydronaphthalene were calculated as the difference $H_s = (\Delta_f H_m^0(\text{g}) - \Sigma_{\text{increments}})$ [14].

In this paper, the additivity rule for the estimation of enthalpy of formation has been examined together with experimental results of thermochemical properties for a number of phenyl-substituted alkenes. These experimental results, together with the data available from the literature, [5,29] provide a coherent understanding of the energetics of phenyl substituted species. The results of the study could also be aimed at an improvement of the group-contribution methodology.

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