Thermodynamic properties of benzyl halides: enthalpies of formation, strain enthalpies, and carbon-halogen bond dissociation enthalpies[†]

Sergey P. Verevkin,* Eugen L. Krasnykh‡ and James S. Wright§

Institute of Physical Chemistry, University of Rostock, Hermannstr. 14, 18051, Rostock, Germany. E-mail: sergey.verevkin@chemie.uni-rostock.de

Received 14th February 2003, Accepted 16th April 2003 First published as an Advance Article on the web 8th May 2003

The molar enthalpies of formation of benzyl halides $PhCH_2-X$, $PhCH(CH_3)-X$, and $PhC(CH_3)_2-X$, where X = F, Cl, Br, and I are in the gaseous state, have been derived by combination of our own thermochemical measurements together with the data available from the literature. These new results have been shown to be internally consistent, and they were used to derive strain enthalpies of benzyl halides as well as for estimation of the carbon–halogen bond dissociation enthalpy in benzyl halides. Strain effects are discussed in terms of deviations of gaseous enthalpies of formation from group additivity rules. Bond dissociation enthalpies (BDE's) of the benzyl halides studied are generally indistinguishable from their alkyl analogs having the same substituent X.

Introduction

Quantification of the bond dissociation enthalpies (BDEs) and energetics of free radicals form a vital part of our understanding of the influence of thermodynamic properties on chemical reactivity. Differences in these energies, while small in percentage terms, obviously have a profound influence on the pathway of chemical reactions. There is a considerable interest in the precise enthalpies of formation of radicals of benzyl derivatives since there are probably no other radicals upon which so many bond energy values depend.¹ Thus, a systematic study of thermochemistry of benzyl derivatives (see Fig. 1) seems to be important for practical and theoretical reasons. The carbon– halogen BDE is defined in the usual way from reaction (1),

$$PhCH_2-Hal \to PhCH_2^{\bullet} + Hal^{\bullet}$$
(1)

according to eqn. (I):

$$\begin{split} \text{BDE}(\text{PhCH}_2\text{-Hal}) &= \Delta_{\text{f}} H^\circ{}_{\text{m}}(\text{g}, \text{PhCH}_2{}^{\bullet}) + \Delta_{\text{f}} H^\circ{}_{\text{m}}(\text{g}, \text{Hal}{}^{\bullet}) \\ &- \Delta_{\text{f}} H^\circ{}_{\text{m}}(\text{g}, \text{PhCH}_2\text{-Hal}) \end{split} \tag{I}$$

Precise values of enthalpies of formation of halogen-radicals $\Delta_{\rm f} H^{\circ}{}_{\rm m}$ (g, Hal[•]) are assigned by CODATA,² as well as the enthalpy of formation of the benzyl radical, $\Delta_{\rm f} H^{\circ}{}_{\rm m}$ (g, PhCH₂[•]) = (207 ± 4) kJ mol⁻¹, which have been recommended recently.³ Hence, bond dissociation enthalpies of benzyl halides, BDE(PhCH₂-Hal), could be derived from eqn. (I), provided that reliable enthalpies of formation, $\Delta_{\rm f} H^{\circ}{}_{\rm m}$ (g, PhCH₂-Hal), of benzyl halides are available.

Unfortunately, thermochemistry of benzyl halides is in disarray. For example, according to Table 1, experimental



Fig. 1 Structures of benzyl derivatives studied.

enthalpies of formation $\Delta_{\rm f} H^{\circ}_{\rm m}$ (l) of benzyl bromide⁴⁻⁸ differ by 15 kJ mol⁻¹ and for benzyl iodide⁷⁻⁹ these values are spread over 17 kJ mol⁻¹. The vaporization enthalpies, $\Delta_{\rm l}^{\rm g} H^{\circ}_{\rm m}$, listed in a recent database⁴⁸ are available only for **1a-d** and most of them are uncertain by ± 2 -4 kJ mol⁻¹. Taking this into account, available gaseous enthalpies of formation, $\Delta_{\rm f} H^{\circ}_{\rm m}$ (g), derived from the sum of contributions $\Delta_{\rm f} H^{\circ}_{\rm m}$ (l) and $\Delta_{\rm l}^{\rm g} H^{\circ}_{\rm m}$, seem to be very uncertain. Thus, it is obvious that thermochemistry of benzyl halides requires additional experimental work. Therefore, we systematically measured¹⁷ a set of molar enthalpies of vaporization $\Delta_{\rm l}^{\rm g} H^{\circ}_{\rm m}$ (298.15 K) for benzyl halides (see Fig. 1) by using the transpiration method¹⁷ and GC-correlation method.^{18,25,46} These new results (see column 3, Table 1) were checked for internal consistency¹⁷ and have

DOI: 10.1039/b301771k

[†] Electronic Supplementary Information (ESI) available: Experimental results (temperature, number of determinations, mole fractions at equilibrium in the liquid phase, x_i , and equilibrium ratios K_x) of the equilibrium study (Tables S1–S4). See http://www.rsc.org/suppdata/ cp/b3/b301771k/

[‡] On leave from the State Technical University, Samara, Russia.

[§] Permanent address: Department of Chemistry, Carleton University, Ottawa, Canada K1S 5B6.

Table 1 Experimental results for benzyl halides at 298.15 K in kJ mol⁻¹ (values selected for the calculation of the gaseous enthalpies of formation are given in italic)

1	$\Delta_{ m f} {H_{ m m}}^{\circ}({ m l})$	$\Delta_{ m l}^{ m g} H_{ m m}^{\circ}$	$\Delta_{ m f} {H_{ m m}}^{\circ}({ m g})$	H_{S}^{g}
	-	5	·	5
Benzyl fluoride (1a)	-172.6 ± 0.7^{10}	44.5 ± 0.4^{11}		
		46.22 ± 0.26^{17}	-126.4 ± 0.7	14.5
Benzyl chloride (1b)	-32.6 ± 2.6^{13}	50.1 ± 0.5^{11}	17.5 ± 2.6	
		51.33 ^k		
		51.1 ± 2.0^{13}	<i>c</i> ·	,
	$(-21.7)^{i}$	50.12 ± 0.27^{17}	$(28.4 \pm 1.5)^{JJ}$	$(6.3)^{l}$
Benzyl bromide (1c)	22.5 ^a	53.14 ^k		
	30.8 ± 3.9^{o}	50.5 ± 0.5^{11}		
	30 ± 14^{5}	47.3 ± 4.2^{48}		
	22.0 ± 4.4^{6}			
	16.2 ± 2.2^{h}	17		
	$(26.3 \pm 4.8)^{c}$	53.27 ± 0.67^{17}	79.6 ± 4.9	6.4
benzyl iodide (1d)	67.7 ^a	50.6 ± 1.4^{11}	127.3 ± 1.3^{9}	
	70.3 ± 1.4^{a}			
	53.0 ± 1.8^{n}	17		
	$(69.0 \pm 2.6)^{c}$	57.38 ± 0.37^{17}	126.4 ± 2.6	0.9
(1-Chloroethyl) benzene (2a)	-58.2 ± 1.8^{14}	52.79 ± 0.24^{17}	-5.4 ± 1.8	5.2
	-60.6 ± 7.2^{e}	17		
(1-Bromoethyl) benzene (2b)	-18.9 ± 7.2^{e}	56.38 ± 0.28^{17}	37.5±7.2	1.5
(1-Iodoethyl) benzene (2c)	$(36.5)^{i}$	59.90 ± 0.35^{17}	$(96.4 \pm 1.5)^{j}$	2.3
α, α -Dimethylbenzyl chloride (3a)	-90.6 ± 4.7^{e}	54.70 ± 0.50^{17}	-35.9 ± 4.8	12.1
	-76.0 ± 3.047	17		
α, α -Dimethylbenzyl bromide (3b)	$-47.2 \pm 5.5^{\circ}$	58.00 ± 0.50^{17}	10.8 ± 5.6	11.2
α, α -Dimethylbenzyl iodide (3c)	(3.1)'	63.30 ± 0.50	$(66.4 \pm 1.5)^{\prime}$	4.4

^{*a*} Value obtained using data from Gellner and Skinner⁸ and results from this work (see text). ^{*b*} Value obtained using data Benson and Buss⁴ and enthalpy of vaporization from this work. ^{*c*} Value has been calculated as the average from the available results; the uncertainty is twice the sd of the mean. ^{*d*} Value obtained using data from Walsh *et al.*⁹ and enthalpy of vaporization from this work. ^{*e*} Derived in this work (see text) using the values of experimental enthalpies of reactions (V–VIII)^{15,16}. ^{*f*} Calculated in this work using eqn. (11). ^{*g*} Strain enthalpy of benzyl derivatives $H_{\rm S} = \{\Delta_{\rm f} H_{\rm m}^{\circ}({\rm g}) - \Sigma$ Benson's increments}. ^{*h*} This result⁷ was disregarded by calculation of the average value. ^{*i*} Assessed in this work from the difference of selected values $\Delta_{\rm f} H_{\rm m}^{\circ}({\rm g}) - \Delta_{\rm g}^{\rm g} H_{\rm m}^{\circ}$ from colmns 4 and 3. ^{*j*} Calculated in this work using eqn. (11) and considered to be more reliable as the existing experimental value. ^{*k*} Calculated in this work using Antoine coefficients from ref. 12 and the procedure developed in ref. 17. ^{*l*} Expected value of strain (see text).

been used in this work for calculation of the gaseous enthalpies of formation $\Delta_f H^{\circ}_m$ (g) of the benzyl derivatives (see column 4, Table 1). Due to the internal consistency and the high precision (*ca.* ±0.5 kJ mol⁻¹) of our new results for $\Delta_l^g H^{\circ}_m$ (298.15 K), the new values of the gaseous enthalpies of formation (column 4, Table 1) should lend themselves to better interpretation.

In order to get insight into reasons for scatter in the database of enthalpies of formation of the benzyl halides in the liquid phase (column 2, Table 1), a careful analysis of the primary experimental data^{4–10} has been performed. This analysis revealed some possible ways for correction of the available results. The first is referred to enthalpies of formation of benzyl bromide **1b** and benzyl iodide **1c**, which were obtained from the calorimetric measurements of enthalpies, $\Delta_r H^{\circ}_m$, of the following reactions:

$$\begin{split} C_6H_5\text{-}CH_2\text{-}Br + H_2O &\rightarrow \text{HBr} + C_6H_5\text{-}CH_2\text{-}OH\\ \Delta_r H^\circ{}_m &= -7.9 \text{ kJ mol}^{-1}; \quad \text{(II)}\\ C_6H_5\text{-}CH_2\text{-}I + H_2O &\rightarrow \text{HI} + C_6H_5\text{-}CH_2\text{-}OH\\ \Delta_r H^\circ{}_m &= 12.6 \text{ kJ mol}^{-1}. \quad \text{(III)} \end{split}$$

There reactions were carefully studied by Gellner and Skinner⁸ in the liquid phase at 298.15 K. Unfortunately, the original values of $\Delta_f H^{\circ}_m$ (l) for **1b** and **1c** derived by Gellner and Skinner⁸ and cited in the literature^{30,48} are not particularly valid, because they were calculated using an uncertain value for benzyl alcohol, C₆H₅-CH₂-OH, measured in the 19th century.¹⁹ A literature search for benzyl alcohol has revealed that, besides some other archival values of ambiguous quantity,^{20,21} there are only two values to merit attention: a recent one from

Papina *et al.*,²² –(154.9 ± 3.0) kJ mol⁻¹, and an older one from Parks *et al.*,²³ –(161.0 ± 1.3) kJ mol⁻¹. Both were measured by combustion calorimetry in the laboratories of impeccable reputation, but their disagreement is larger than the experimental uncertainties! In order to resolve this contradiction, we decided to obtain the enthalpy of formation of benzyl alcohol in an independent way. Indeed, a study of the chemical equilibrium in the reactive system



gives the value of the reaction enthalpy, $\Delta_r H^{\circ}_m$ (l) which, according to the second law of thermodynamics, could serve to obtain the enthalpy of formation, $\Delta_f H^{\circ}_m$ (l) of benzyl alcohol **1e**, provided that enthalpies of formation of the other reaction participants (*tert*-amyl benzyl ether **1f** and 2-methylbutene-2) are known. The enthalpy of formation of 2-methylbutene-2 is well established.²⁴ Thus, combustion experiments on *tert*-amyl benzyl ether **1f** should provide the knowledge of the enthalpy of formation of benzyl alcohol **1e** independently, and will help to resolve the contradiction between the two values available from the literature.^{22,23} Then, having established a reliable enthalpy of formation for benzyl alcohol, the results from Gellner and Skinner⁸ can be corrected and used for estimation of reliable values of enthalpies of formation of the bromide **1b** and iodide **1c**.

The second helpful way to understand trends in thermochemistry of benzyl halides 1a-d is to consider their parent compounds, such as α -methyl-substituted benzyl halides **2a–c**, and α,α -dimethyl-substituted benzyl halides (cumyl halides) **3a–c**. Thus, in this work we have derived enthalpies of formation, $\Delta_f H^{\circ}_m$ (l), of the benzyl derivatives **2** and **3** (see Table 1) using experimental results from equilibrium studies.^{15,16} Hence, our additional efforts provide a broader data set on the gaseous enthalpies of formation $\Delta_f H^{\circ}_m$ (g) of benzyl derivatives, which can be used to derive carbon–halogen bond dissociation enthalpies.

Experimental

Materials

Benzyl alcohol and 2-methylbutene-2 (2MB2) were of commercial origin. *Tert*-amyl benzyl ether (1f) was synthesised *via* alkylation of benzyl alcohol with 2MB2 [reaction (IV)] in the presence of a catalytic amount of cation exchange resin in H^+ form (Amberlist 15, Aldrich) at room temperature and was purified by repeated distillation under reduced pressure. GC analysis of the sample for thermochemical measurements gave a purity >99.99%.

Chemical equilibrium study

The chemical equilibrium of [reaction (IV)] was studied in the liquid phase in the temperature range (303 to 371 K) using glass vials with screw caps. Vials were filled with the initial liquid mixture of alkanols and 2-methylbutene-2. Cationexchange resin Amberlist 15 (Aldrich) in H⁺ form was added as a heterogeneous catalyst. Each vial was thermostatted at $T_i \pm 0.1$ K and periodically shaken. After definite time intervals the vial was cooled rapidly in ice and opened. A sample for GC analysis was taken from the liquid phase using a syringe. The thermostatting of the vial then proceeded at the same temperature. Samples were taken successively until no further change of composition was observed, indicating that the chemical equilibrium was established. The equilibrium ratio K_x was obtained from the current concentrations of the reaction participants, which were analysed with a Hewlett-Packard gas chromatograph 5890 Series II equipped with a flame ionisation detector and a capillary column HP-5. The response factors of all reagents were determined using calibration mixtures of the corresponding components prepared gravimetrically.

The experimental results (temperature, number of determinations, mole fractions at equilibrium in the liquid phase, x_i , and equilibrium ratios K_x) of the equilibrium study are deposited as electronical supplementary information.[†] It was well documented in our previous work²⁶ that alkyl ether synthesis mixtures behave non-ideally, and that the equilibrium ratio K_x strongly depends on the composition of the equilibrium mixture. However, it has been observed²⁶ for systems similar to reaction (IV) that K_x -values are almost independent of the mole fraction of alkanol if $x_{AlkOH} > 0.5$. For such systems it has been proven that the equilibrium ratio $K_x \approx K_a$ (thermodynamic equilibrium constant) for mixtures with $x_{AlkOH} >$ 0.5, by comparison of the results of equilibrium studies in the gaseous and liquid phases simultaneously.²⁶ Taking this experience into account, we investigated reaction (IV) in an excess of alcohols (the summarised mole amount of benzyl alkohol and butanol was $x_{AlkOH} > 0.5$.) Experimental values of K_x were approximated as a function of temperature by the linear equation $\ln K_a = a + b \cdot (T/K)^{-1}$, using a least squares fit. The slopes of these lines when multiplied by the gas constant yield the enthalpy of reaction (IV) $\Delta_r H^{\circ}{}_m$ and the intercept gives the entropy of reaction $\Delta_r S^\circ{}_m.$ Numerical results are as follows:

$$\ln K_{\rm a} = -5.14 \cdot (1000/T) + 18.67$$

$$\begin{split} \Delta_{\rm r} H^\circ{}_{\rm m} \ ({\rm l}) &= (42.7\pm0.8) \ {\rm kJ} \ {\rm mol}^{-1}; \\ \Delta_{\rm r} S^\circ{}_{\rm m} \ ({\rm l}) &= (155.2\pm2.4) \ {\rm J} \ {\rm K}^{-1} \ {\rm mol}^{-1} \end{split}$$

In spite of the fact that equilibrium studies have been performed at elevated temperatures (303 to 371 K), any corrections of the reaction enthalpies are negligible²⁶ when taking into account the individual error bars of *ca*. 1-2 kJ mol⁻¹ typical for the equilibrium measurements. In the above, it was assumed that the change in the enthalpy of reaction is negligible on passing from the average temperature of the experimental range to T = 298.15 K.

Combustion calorimetry

The pure sample of *tert*-amyl benzyl ether 1f was obtained by repeated distillation under N2 using a spinning-band column at reduced pressure. No impurities could be detected in tert-amyl benzyl ether by GC. For combustion experiments the purified liquid samples were dried over molecular sieves and distilled once more before combustion. This procedure provided colourless material, and the absence of water was shown by Karl Fischer titration. For measurements of the energies of combustion of the benzyl ethers a rotating-bomb calorimeter described elsewhere²⁸ was used. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none was detected. For converting the energy of the actual bomb process to that of an isothermal process, and reducing to standard states the conventional procedure²⁹ was applied. Results of a typical combustion experiment for 1f and the mean values of the standard specific energies of combustion $\Delta_c u^{\circ}$, together with their standard deviations, are are deposited as electronical supplementary information.[†] We obtained the resulting value $\Delta_{\rm f} H^{\circ}{}_{\rm m}$ (l) = -(263.8 ± 3.0) kJ mol^{-1} (the uncertainty assigned is twice the overall standard deviation and includes the uncertainties from calibration, from the combustion energies of the auxiliary materials, and the uncertainties of the enthalpies of formation of the combustion products H₂O and CO₂).

Results and discussion

Enthalpy of formation of benzyl alcohol

We investigated the chemical equilibrium of reaction (IV) of synthesis of *tert*-amyl benzyl ether from benzyl alcohol and 2-methylbutene-2 and derived the enthalpy of this reaction in the liquid phase. The enthalpy of formation $\Delta_f H^{\circ}_m$ (l) of *tert*-amyl benzyl ether at 298.15 K was measured by means of combustion calorimetry in this work. Using $\Delta_f H^{\circ}_m$ (l) = $-(68.1 \pm 1.3)$ kJ mol⁻¹ for 2MB2 available in literature²⁴ we calculated the enthalpy of formation of benzyl alcohol **1e** in the liquid phase:

$$\begin{aligned} \Delta_{\rm f} H^{\circ}{}_{\rm m} \ ({\rm l})_{(1{\rm e})} &= \Delta_{\rm r} H^{\circ}{}_{\rm m} \ ({\rm l}) - \Delta_{\rm f} H^{\circ}{}_{\rm m} \ ({\rm l})_{(2{\rm MB2})} + \Delta_{\rm f} H^{\circ}{}_{\rm m} \ ({\rm l})_{(1{\rm f})} \\ &= -(153.5 \pm 3.4) \ {\rm kJ \ mol^{-1}}. \end{aligned}$$

This value is in very close agreement to the recent result from Papina *et al.*²² $-(154.9 \pm 3.0)$ kJ mol⁻¹ measured by combustion calorimetry and inconsistent with the older one from Parks *et al.*²³ Thus, our value helps to resolve the contradiction between two available results in the literature. Taking into account the close agreement of our and Papina *et al.*'s²² result on $\Delta_f H^{\circ}_m$ (l) of benzyl alcohol, we prefer the more precise and direct result from Papina *et al.*²²

Enthalpies of formation of benzyl bromide (1c) and benzyl iodide (1d). Gellner and Skinner⁸ measured enthalpies of the hydration reactions (II) and (III) calorimetrically at 298.15 K. Having established in this work a more reliable $\Delta_f H^{\circ}_m$ (l)

of benzyl alcohol, we were able to derive new values (see Table 1) of $\Delta_{\rm f} H^{\circ}_{\rm m}$ (l) of benzyl bromide (1c) and benzyl iodide (1d) using calorimetric results⁸ and the chosen $\Delta_{\rm f} H^{\circ}{}_{\rm m}$ (l) = $-(154.9 \pm 3.0)$ kJ mol⁻¹ for benzyl alcohol.²² A summary of the results available for the benzyl halides is presented in Table 1. As can be seen from this table, enthalpies of benzyl bromide (1c) and benzyl iodide (1d) derived in this work are in agreement with those already available from the literature, within the range of their experimental uncertainties. Thus, for both compounds the average values of $\Delta_{\rm f} H^{\circ}{}_{\rm m}$ (l) have been calculated and used to derive gaseous enthalpies of formation $\Delta_{\rm f} H^{\circ}{}_{\rm m}$ (l) (column 4, Table 1). It is worth mentioning that experimental results for $\Delta_{\rm f} H^{\circ}{}_{\rm m}$ (l) of 1c and 1d obtained by Ashcroft et al.⁷ from calorimetrically measured hydrogenation enthalpies of benzyl halides are systematically lower by over 10 kJ mol⁻¹. An explanation of this fact is still evasive, but it might be due to incorrect calibration of their device. Thus, results from this work were disregarded by calculation of the average values given in Table 1.

Enthalpies of formation of benzyl derivatives 2 and 3. Kovsel^{15,16} investigated the equilibrium of hydrohalogenation of styrene and α -methyl-styrene in the liquid phase using SnCl₄ and CuCl as catalyst. As those results are not readily available, they are presented briefly below:

C₆H₅-CH=CH₂ + HCl ↔ C₆H₅-CHCI-CH₃;
T-range: 353-413 K Δ_f
$$H^{\circ}_{m} = -55.7 \pm 7.1 \text{ kJ mol}^{-1};$$

Δ_f $S^{\circ}_{m} = -125.3 \pm 14.7 \text{ J mol}^{-1} \text{ K}^{-1}$ (V)

$$\begin{split} & C_{6}H_{5}\text{-}CH\text{=}CH_{2} + HBr \leftrightarrow C_{6}H_{5}\text{-}CHBr\text{-}CH_{3}; \\ & T\text{-range: } 383\text{-}413 \text{ K } \Delta_{f}H^{\circ}{}_{m} = -69.1 \pm 7.1 \text{ kJ mol}^{-1}; \\ & \Delta_{f}S^{\circ}{}_{m} = -125.7 \pm 14.7 \text{ J mol}^{-1} \text{ K}^{-1} \end{split}$$
 (VI)

C₆H₅−C(CH₃)=CH₂ + HCl ↔ C₆H₅−C(CH₃)Cl−CH₃;
T-range: 333–413 K
$$\Delta_{\rm f} H^{\circ}{}_{\rm m} = -52.0 \pm 4.6 \text{ kJ mol}^{-1};$$

 $\Delta_{\rm f} S^{\circ}{}_{\rm m} = -130.3 \pm 13.0 \text{ J mol}^{-1} \text{ K}^{-1}$ (VII)

 $C_6H_5-C(CH_3)=CH_2+HBr \leftrightarrow C_6H_5-C(CH_3)Br-CH_3;$

T-range: 363–413 K
$$\Delta_{\rm f} H^{\circ}{}_{\rm m} = -63.7 \pm 5.4 \text{ kJ mol}^{-1}$$
;

$$\Delta_{\rm f} S^{\circ}{}_{\rm m} = -134.1 \pm 13.8 \ {\rm J} \ {\rm mol}^{-1} \ {\rm K}^{-1} \tag{VIII}$$

In spite of the fact that equilibrium studies have been performed at elevated temperatures, corrections of the reaction enthalpies to the reference temperature 298.15 K are assessed as not larger than 1.5 to 2 kJ mol⁻¹, and match the individual error bars of the equilibrium measurements. In further calculations it was assumed that the enthalpy of reaction hardly changes on passing from the average temperature of the experimental range to T = 298.15 K.

Enthalpies of formation of the benzyl derivatives **2** and **3** were calculated using the enthalpies of reactions (V)–(VIII). For this purpose some additional thermochemical data have been involved: enthalpy of formation $\Delta_f H^{\circ}_m$ (I) = (103.8 ± 1.1) kJ mol⁻¹ for styrene,³⁰ and $\Delta_f H^{\circ}_m$ (I) = (70.07 ± 0.82) kJ mol⁻¹ for α -methyl-styrene.³¹ Only the gaseous enthalpy of formation for HCl $\Delta_f H^{\circ}_m$ (g) = –(92.31 ± 0.13) kJ mol⁻¹ and for HBr $\Delta_f H^{\circ}_m$ (g) = –(36.38 ± 0.17) kJ mol⁻¹ were assigned by CODATA.² However, in order to obtain their $\Delta_f H^{\circ}_m$ (I) in the liquid phase, vaporization enthalpies, $\Delta_I^g H^{\circ}_m$ are required. We calculated the latter using parameters of the Antoine equation for vapor pressure from a literature compilation¹² with the help of the equation:³²

$$\Delta_1^{\mathrm{g}} H^{\circ}_{\mathrm{m}} (\mathrm{J} \mathrm{mol}^{-1}) = (2.3 \cdot R \cdot \Delta Z \cdot B \cdot T^2) \cdot (T+C)^{-2}$$

where $R = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$; *B* and *C* are Antoine equation parameters; ΔZ is the difference in compression factors of vapor and liquid ($\Delta Z \approx 1$ was calculated using the Haagen-

macher equation³² at the reference temperature 298.15 K). The enthalpies of vaporization estimated using this procedure were $\Delta_l^g H_m^{\circ}$ (298.15 K) = (16.4 ± 1.0) kJ mol⁻¹ for HCl and $\Delta_l^g H_m^{\circ}$ (298.15 K) = (17.2 ± 1.0) kJ mol⁻¹ for HBr. Thus, the desired values $\Delta_f H_m^{\circ}$ (l) = -(108.7 ± 1.0) kJ mol⁻¹ for HCl $\Delta_f H_m^{\circ}$ (l) = -(53.6 ± 1.0) kJ mol⁻¹ for HBr were calculated as the difference between $\Delta_f H_m^{\circ}$ (g) and $\Delta_l^g H_m^{\circ}$. Enthalpies of formation, $\Delta_f H_m^{\circ}$ (l), of the benzyl derivatives **2a–b** and **3a–b** were calculated using the enthalpies of reactions (V)–(VIII) and enthalpies of formation of the reaction participants are listed in Table 1. The validity of the procedure applied to derive enthalpies of formation of **2a–b** and **3a–b** is confirmed by the close agreement of our result for **2a**, $\Delta_f H_m^{\circ}$ (l)_{**2a**} = -(60.6 ± 7.2) kJ mol⁻¹, and that measured by combustion calorimetry:¹⁴ $\Delta_f H_m^{\circ}$ (l)_{**2a**} = -(58.2 ± 1.8) kJ mol⁻¹.

For α, α -dimethylbenzyl chloride (**3a**) the value of $\Delta_{\rm f} H^{\circ}_{\rm m}$ (l)_{**3a**} = $-(76.0 \pm 3.0)$ kJ mol⁻¹ was obtained from the calorimetrically measured enthalpy of hydrochlorination of α methyl-styrene⁴⁷ in solvent (methylene chloride). This value is in disagreement with the result obtained in this work under neat conditions, $-(90.6 \pm 4.7)$ kJ mol⁻¹. The disagreement might be due to possible rapid polymerisation of α -methylstyrene in the conditions of calorimetric study.⁴⁷ However, the consistency of thermochemical result for **2a**, obtained from the equilibrium study^{15,16} and those from combustion calorimetry¹⁴ allowed us to give preference to the value derived in this work.

Correlation of $\Delta_{f} H^{\circ}{}_{m}$ (g) of benzyl halides with $\Delta_{f} H^{\circ}{}_{m}$ (g) of alkyl analogs. Gaseous enthalpies of formation $\Delta_f H^{\circ}_m$ (g) of benzyl derivatives 1-3 were derived in this work as the sum of the selected $\Delta_{\rm f} H^{\circ}{}_{\rm m}$ (l) and enthalpies of vaporization listed in Table 1. Taking into account the high chemical reactivity and thermal lability of the benzyl derivatives, which could aggravate thermochemical measurements, proof of the reliability of results derived in this work would be desirable. The set of $\Delta_{\rm f} H^{\circ}{}_{\rm m}$ (g) of the benzyl derivatives derived in this work could be checked for internal consistency using gaseous enthalpies of formation of alkyl halides. In contrast to benzyl halides, experimental thermochemical data on alkyl halides are well established.³⁰ The set of $\Delta_{f}H^{\circ}{}_{m}$ (g) of alkyl halides C_1-C_4 recommended by Pedley *et al.*³⁰ has been successfully checked for internal consistency in the review by Slayden et al.⁴⁹ recently. We used their set of selected values $\Delta_{\rm f} H^\circ{}_{\rm m}$ (g) of alkyl halides C_2 - C_4 (see electronic supplementary information[†]) for correlation with our results on benzyl halides.

Now let us consider structures of the benzyl derivatives presented in Fig. 1. It is obvious, that benzyl derivatives (1) are parent to the structure of the ethyl derivatives C_2H_5 -X, for example, PhCH₂-Cl (1b) and C_2H_5 -Cl. Benzyl derivatives (2) are parent to the structure of the isopropyl derivatives iso- C_3H_7 -X. Benzyl derivatives (3) are parent to the structure of the *tert*-butyl derivatives *tert*-C₄H₉-X. Thus, the correlation of the enthalpies of formation of 1–3 with those of alkyl derivatives alkyl-X, where X = halogen should be linear if the data used for the correlation are reliable. As can be seen from Fig. 2, the data for benzyl and alkyl derivatives fit very well (except for benzyl chloride) in the linear correlation:

$$\begin{aligned} \Delta_{\rm f} H^{\circ}{}_{\rm m} & ({\rm g}, 298.15 \text{ K}, \text{ benzyl-X})/\text{kJ mol}^{-1} \\ &= (0.947 \pm 0.014) \cdot [\Delta_{\rm f} H^{\circ}{}_{\rm m} & ({\rm g}, 298.15 \text{ K}, \text{ alkyl-X})] \\ &+ (134.5 \pm 1.1) \end{aligned} \tag{11}$$

Such a relationship with correlation coefficient (r = 0.999) is evidence of the internal consistency of the experimental results for the benzyl derivatives listed in Table 1; only $\Delta_f H^{\circ}_m$ (g) of benzyl chloride (**1b**) is definitely outside this linear correlation. However, there are no apparent reasons for such deviation and taking into account that its enthalpy of formation (see Table 1)



Fig. 2 Relation between enthalpies of formation of alkyl halides and benzyl halides (in kJ mol⁻¹). ○, ● Relation between $\Delta_{\rm f} H^0_{\rm (g)}$ of C₂H₅-X and $\Delta_{\rm f} H^0_{\rm (g)}$ PhCH₂-X; ▲ relation between $\Delta_{\rm f} H^0_{\rm (g)}$ of C₂H₇-X and $\Delta_{\rm f} H^0_{\rm (g)}$ PhCH(CH₃)-X; ■ relation between $\Delta_{\rm f} H^0_{\rm (g)}$ of C₄H₉-X and $\Delta_{\rm f} H^0_{\rm (g)}$ PhCH(CH₃)₂-X.

is known only from a single work,¹³ it seems to be justifiable that benzyl chloride belongs to the line defined by eqn. (II). That is why $\Delta_f H^{\circ}_{m}$ (g) = (28.4±1.5) kJ mol⁻¹ of **1b**, assessed by using eqn. (11) and the enthalpy of formation of C₂H₅-Cl, seems to be more reliable than the experimentally measured value $\Delta_f H^{\circ}_{m}$ (g) = (17.5±2.6) kJ mol⁻¹ presented in Table 1. In addition,, enthalpies of formation of compounds **2c** and **3c** have been estimated using eqn. (11) and $\Delta_f H^{\circ}_{m}$ (g) of the appropriate alkyl iodides³⁰ and are presented in Table 1.

Strain enthalpies H_S of benzyl derivatives. Another possible way to establish consistency of thermochemical properties of benzyl derivatives is by comparison of strain enthalpies, which can be derived from their gaseous molar enthalpies of formation at 298.15 K (Table 1). Indeed, the benzyl derivatives **1a–d**, **2a–c**, and **3a–c** listed in Table 1 present a typical example of similarly shaped molecules, where halogen is attached to the appropriate benzyl moiety. Hence the strain, H_S , of a molecule is expected to provide insight into the energetic interactions of a halogen with the phenyl ring attached to the geminal C-atom.

We define the strain enthalpy $H_{\rm S}$ of a molecule as the difference between the experimental enthalpy of formation $\Delta_{\rm f} H^{\circ}{}_{\rm m}$ (g) and the calculated sum of the Benson type increments^{33,34,27} for this molecule. By using these group-additivity parameters and the values of $\Delta_{\rm f} H^{\circ}{}_{\rm m}$ (g) of benzyl derivatives (Table 1), the values of strain enthalpies $H_{\rm S} = \Delta_{\rm f} H^{\circ}{}_{\rm m}$ (g) $-\Sigma$ increments} have been estimated (Table 1).

Almost all of the benzyl derivatives listed in Table 1 are strained. Understanding strain in benzyl derivatives is aided by comparison to the strain in similarly shaped alkylbenzenes, e.g. ethylbenzene, isopropylbenzene and tert-butylbenzene. Enthalpies of formation $\Delta_{\rm f} H^{\circ}{}_{\rm m}$ (g) and strain enthalpies $H_{\rm S}$ of ethylbenzene (29.9 kJ mol⁻¹ and 0.6 kJ mol⁻¹) isopropylbenzene; (4.0 kJ mol⁻¹ and 5.6 kJ mol⁻¹), and tert-butylbenzene; $(-24.4 \text{ kJ mol}^{-1} \text{ and } 9.4 \text{ kJ mol}^{-1})$ are known from the literature. The enthalpies of formation of these compounds were taken from Pedley *et al.*,³⁰ except for *tert*-butylbenzene.³⁵ These alkylbenzenes show relevant structural patterns of strain in the benzyl derivatives studied. Their strain enthalpies describe the intrinsic strain of the alkylbenzenes due to steric repulsions of the alkyl groups and the benzene ring attached to the tertiary or quaternary carbon atom. Comparison of strain energies in the benzyl derivatives with those of alkylbenzenes allows the derivation of the strain effects directly. The values $H_{\rm S}$ of the benzyl derivatives could be interpreted



Fig. 3 Conformational preferences of benzyl-X compounds.

as the sum of excess geminal interactions of the phenyl and the halogen on the central C-atom.

Let us consider the row of the benzyl derivatives **1a-d** which are parent to ethylbenzene. Ethylbenzene itself is strainless. However, benzyl fluoride exhibits the most noticeable interaction, amounting to 14.5 kJ mol⁻¹. A plausible explanation of the observed destabilization of benzyl fluoride was suggested by Penner et al.³⁶ By means of spectral analyses and ab initio methods they determined the conformational preferences of some benzyl-X derivatives with the aim of establishing whether stabilising interactions enhance the conformational preference for the perpendicular structure (see Fig. 3). Except for X = F, compounds studied [X = Cl, SH, SMe, S(O)Me]adopted mainly the conformation in which the C-H bond is perpendicular to the plain of the benzene ring. The authors proposed therefore the existence of a "benzylic anomeric effect", and that its magnitude is S(O)Me > Cl > SH, SMe > F. The exceptional planar conformation of benzyl fluoride determined by Penner *et al.*³⁶ and the profound destabilization of 14.5 kJ mol⁻¹ for this molecule established in our thermochemical study are evidence that the possible "benzylic anomeric effect" is destroyed by a dipole-dipole interaction between the phenyl and fluorine substituents. A similar explanation seems to be acceptable for the less profound destabilization (*ca*. 6 kJ mol⁻¹) observed in benzyl chloride and benzyl bromide, as well as for the nearly strainless ($H_{\rm S}=0.9~{\rm kJ}$ mol^{-1}) benzyl iodide.

Benzyl derivatives **2a–c**, which are parent to the isopropylbenzene ($H_{\rm S} = 5.6 \text{ kJ mol}^{-1}$) also show similar strain ($H_{\rm S} =$ 1.5 to 5.2 kJ mol⁻¹). Hence, it is reasonable to presume that methyl groups are able to disorder the optimal orientation of dipoles in the suggested planar conformation (see Fig. 3) of α -substituted benzyl derivatives **2a–c** and no additional destabilization will arise in these molecules.

Benzyl derivatives 3a-c are strained by *ca*. 10 kJ mol⁻¹ (see Table 1) and the observed amount of destabilization could no doubt be attributed to the inherent strain due to the steric repulsions of methyl groups and the benzene ring attached to the central quaternary carbon atom, as in the similarly shaped *tert*-butylbenzene with $H_{\rm S} = 9.4$ kJ mol⁻¹. Thus, strain enthalpies of the benzyl derivatives discussed above in terms of deviation from additivity rules reveal reasonable similarities within the structural pattern 1, 2, or 3, and establish consistency of values for $\Delta_f H^o_{\rm m}$ (g) derived in this work.

Calculation of the bond dissociation enthalpies of benzyl halides. Benzyl halides are very reactive and thermolabile, which is why these compounds are often used for determination of the bond dissociation enthalpy (BDE).^{37,38} In this work, gaseous enthalpies of formation of benzyl halides have been derived according to eqn. (1) and listed in Table 1. Enthalpies of formation of halogen-radicals $\Delta_f H^{\circ}_m$ (g, Hal^{*}) were assigned by CODATA.² Enthalpies of formation of benzyl-radicals: PhCH₂[•], PhCH(CH₃)[•], and PhC(CH₃)₂[•] were recommended in the recent literature.^{3,39} Thus, using these data, the values of dissociation enthalpies of the C–Hal bond in the benzyl halides 1–3 were estimated and are presented in Table 2.

The BDE (PhCH₂F) = 412.8 kJ mol⁻¹ derived in this work is in excellent agreement with the experimental value from

Table 2 Comparison of the BDE of Alkyl Halides and Benzyl Halides

	BDE/kJ mol ⁻¹				
	F	Cl	Br	Ι	
CH ₃ CH ₂ -X	451.5 ^a	350.2 ^a	290.8 ^a	231.4 ^{<i>a</i>}	
$PhCH_2-X^b$	412.8 ± 4.1	299.9 ± 4.3	239.3 ± 6.3	187.8 ± 4.8	
(CH ₃) ₂ CH-X	453.1 ^a	346.4 ^{<i>a</i>}	291.6 ^a	227.2^{a}	
PhCH(CH ₃)-X ^c		292.4 ± 4.4	240.1 ± 8.2	176.1 ± 4.3	
$(CH_3)_3C-X^d$	_	351.6 ± 3.8	292.4 ± 3.5	226.9 ± 4.5	
$PhC(CH_3)_2-X^e$	_	292.8 ± 6.3	236.7 ± 6.9	176.0 ± 4.3	

Zavitsas⁴⁰ (412.5 \pm 8.4) kJ mol⁻¹. However, theoretical studies of the BDE in benzyl fluoride are in disagreement. Earlier B3LYP-based calculations³⁷ of this quantity gave 406.7 kJ mol⁻¹ and a value of 402.5 kJ mol⁻¹ was calculated³⁷ by the semiempirical AM1 method. The most recent result of 417.1 kJ mol⁻¹ was calculated using the lowest level method (LLM) of DiLabio et al., which is a hybrid of the B3LYP method (for the energy) and the AM1 method (for geometry and frequency).³⁸ The BDE (PhCH₂–Cl) = 299.9 kJ mol⁻ derived in this work may be compared with experimental values 289.1 kJ mol⁻¹ and 299.6 kJ mol⁻¹ (electrochemical measurements)⁴¹ and calculated values $287.0 \text{ kJ mol}^{-1}$ (B3LYP),³⁷ 278.6 kJ mol⁻¹(AM1),³⁷ and 296.2 kJ mol⁻¹ (LLM).³⁸ For benzyl bromide, our derived C–Br BDE is 239.3 kJ mol⁻¹, which may be compared with the following experimental values: 233.9 or 222.2 kJ mol⁻¹ (electrochemical measurements),⁴¹ 254.0 kJ mol⁻¹ (PAC measurements),⁴² and 254.8 kJ mol⁻¹ (thermolysis of the benzyl bromide in the gas phase).⁴² Calculated values are 238.9 kJ mol⁻¹ (B3LYP),³⁷ 232.6 kJ mol⁻¹ (AM1),³⁷ and 257.7 kJ mol⁻¹ (LLM).³⁸ The BDE (PhCH₂–I) = 187.8 kJ mol⁻¹ derived in this work is close to another experimental value of 190.0 kJ mol⁻¹ from shock-wave dissociation measurements.⁴³

Comparison of the BDE's of alkyl halides and benzyl halides, presented in Table 2, indicates that the benzylic bond strength is substantially lower ($30-60 \text{ kJ mol}^{-1}$) than those in the similarly shaped alkyl analogues. However, the general trends, such as the weakest bond in the I-derivatives and the strongest bond in the F-derivatives, remain common for both chemical families. It can also be seen that values for the BDE of PhCH₂-X, PhCH(CH₃)-X and PhC(CH₃)₂-X, are generally independent of the branching of benzylic C-atom (CH₂, CH, or C) similarly with their alkyl analogues having the same substituent X. This fact again supports the consistency of the thermochemical data derived in this work and involved in the estimation of the BDE of the benzyl derivatives.

An internally consistent set of theoretical values of the BDE. It is difficult to be completely confident about trends in bond-

Table 3A consistent set of theoretically calculated values, using the
LLM method (values in parentheses were reported earlier using the
same (LLM) method38

	BDE/kJ mol ⁻¹			
	F	Cl	Br	
CH ₃ -X	462.1 (461.9)	354.9 (354.8)	312.9 (313.4)	
CH ₃ CH ₂ -X	473.7	356.8	311.3	
(CH ₃) ₂ CH-X	482.5	358.9	310.3	
(CH ₃) ₃ C-X	483.7	359.0	304.2	
PhCH ₂ -X	416.6 (417.1)	299.6 (296.2)	256.5 (257.7)	
Ph(CH ₃)CH-X	425.1	297.8	250.8	
Ph(CH ₃) ₂ C-X	434.0	294.8	243.6	

ing, when data are drawn from many different sources. Here we present an internally consistent set of BDEs for the alkyl and benzyl halides, all calculated (or recalculated) using the LLM method. These values are all shown in Table 3, where earlier values³⁸ obtained using the same LLM method are shown in parentheses. Agreement with earlier values is usually within 1 kJ mol⁻¹ except for benzyl chloride, which differs by over 3 kJ mol⁻¹. Such differences can arise from different conformations, so it is necessary to specify the AM1-preferred conformer used in the calculation.

For benzyl fluoride, there are AM1 minima at the planar and perpendicular positions of the F atom, relative to the phenyl ring. The planar conformer is favoured by 3.8 kJ mol⁻¹, in agreement with the experiment. For benzyl chloride and benzyl bromide, only the perpendicular conformer (C–X bond perpendicular to the ring) is stable. For PhCH(CH₃)X, the F-atom lies in the ring plane, whereas the Cl and Br atoms have dihedral angle 60° with the ring. For PhC(CH₃)₂X, the F atom is in the ring plane. In the chloride, the methyl carbon lies in the ring plane and the C–Cl bond has dihedral angle 60°. (There is another conformer with the Cl atom planar, but this is less stable by 4 kJ mol⁻¹). The bromide is identical to the chloride, with dihedral angle 60° and two conformers.

Table 3 shows that there are systematic trends for BDEs in the alkyl halides and in the benzyl halides. In particular, increasing methyl substitution in the alkyl halides: (i) causes the C–F BDE to increase, although diminishing returns are reached for the tertiary methyl group, (ii) causes the C–Cl BDE to increase slightly then reach a plateau, and (iii) causes the C–Br BDE to decrease slightly. The point for $(CH_3)_3C$ –Br seems anomalous but the other trends are smooth. Increasing methyl substitution in the benzyl halides (i) causes the C–F BDE to increase; (ii) causes the C–Cl BDE to decrease (slightly); and (iii) causes the C–Br BDE to decrease (significantly) with increasing substitution.

The agreement between our calculated BDE values and the experimental values is essentially within experimental error for C–F and C–Cl bonds, although there are larger errors for C–Br bonds. There are several possible reasons for this in the theoretical calculation: (i) The AM1 geometries and frequencies for C–Br do not contain as many molecules in the calibration set for AM1, hence an inferior set of AM1 parameters; (ii) the 6-311+G(2d,2p) basis set may be inadequate for atoms with atomic number as high as Br; (iii) spin–orbit coupling may play a role in calculation of the Br radical especially. Without extensive testing it is difficult to be sure which of these effects is dominant, so we consider it reasonable to expect errors to increase as we calculate values for Br and I.

Conclusions

In recent years considerable activity has taken place with respect to the estimation of the $BDE's^{37,38}$ and enthalpies of

Acknowledgements

S. V. expresses his gratitude to Prof. Dr C. Rüchardt and Dr H.-D. Beckhaus for supporting the combustion experiments and for the exceedingly creative atmosphere in their laboratory. One of us (E.K.) gratefully acknowledges a research scholarship from the DAAD (Deutscher Akademischer Austauschdienst).

References

- D. F. McMillen and D. M. Golden, Annu. Rev. Phys. Chem., 1 1982, 33, 493.
- 2 CODATA Key Values for Thermodynamics, ed. J. D. Cox, D. D. Wagman and V. A. Medvedev, Hemisphere, New York, 1989
- 3 W. Tsang, in Energetics of Organic Free Radicals, ed. J. A. Martinho Simoes, A. Greenberg and J. F. Liebman, Blackie Academic and Professional, London, 1996, pp. 22–58.
- S. W. Benson and J. H. Buss, J. Phys. Chem., 1957, 61, 104. 4
- P. A. Fowell and C. T. Mortimer, J. Chem. Soc., 1961, 3793.
- T. Holm, J. Organomet. Chem., 1973, 56, 87.
- S. J. Ashcroft, A. S. Carson and J. B. Pedley, Trans. Faraday Soc., 7 1963, 59, 2713.
- O. H. Gellner and H. A. Skinner, J. Chem. Soc., 1949, 1145. 8
- R. Walsh, D. M. Golden and S. W. Benson, J. Am. Chem. Soc., 9 1966, 88, 650.
- F. Schaffer, S. P. Verevkin, H.-J. Rieger, H.-D. Beckhaus and 10 Rüchardt, Liebigs Ann. Chem., 1997, 1, 1333
- S. J. Ashcroft, J. Chem. Eng. Data, 1976, **21**, 397. D. R. Stull, Ind. Eng. Chem., 1947, **39**, 517.
- 12
- 13
- F. W. Kirkbride, J. Appl. Chem., 1956, 6, 11.
 A. T. Hu and G. C. Sinke, J. Chem. Thermodyn., 1969, 1, 507. 14
- E. N. Kovzel, PhD Thesis, Saratov State University, Saratov, 15 USSR, 1981.
- 16 T. N. Nesterova, E. N. Kovzel, S. Ya. Karaseva, A. M. Rozhnov, Heats of reaction of the hydrohalogenation of styrene and α-methylstyrene, Vses. Konf. Kalorim., Rasshir. Tezisy Dokl. 7th, Acad. Nauk USSR, Moscow, 1977, p. 132.
- E. L. Krasnykh, T. V. Vasiltsova, S. P. Verevkin and A. Heintz, 17 J. Chem. Eng. Data, 2002, 47, 1372.
- S. P. Verevkin, E. L. Krasnykh, T. V. Vasiltsova and A. Heintz, 18 J. Chem. Eng. Data, 2003, 48in press.
- 19 F. Stohmann, Z. Phys. Chem. Stoichiom. Verwandtschaftle, 1890, 6, 334

- P. Landrieu, F. Baylocq and J. R. Johnson, Bull. Soc. Chim. Fr., 20 1929 45 36
- 21 M. Schmidlin, Ann. Chim. Phys., 1906, 1, 195.
- 22 T. S. Papina, S. M. Pimenova, V. A. Luk'yanova and V. P. Kolesov, Russ. J. Phys. Chem. Transl. of Zh. Fiz. Khim., 1995, 69, 1951. In original 2148.
- G. S. Parks, K. E. Manchester and L. M. Vaughan, J. Chem. 23 Phys., 1954, 22, 2089.
- 24 W. D. Good and N. K. Smith, J. Chem. Thermodyn., 1979, 11. 111.
- 25 H. M. McNair and E. J. Bonelli, Basic Gas Chromatography, Consolidated Printers, , Oakling, California, 1967.
- 26 A. Heintz and S. P. Verevkin, Fluid Phase Equilib., 2001, 179, 85. 27 E. S. Domalski and E. D. Hearing, J. Phys. Chem. Ref. Data, 1993. 22. 805-1159.
- 28 H.-D. Beckhaus, G. Kratt, K. Lay, J. Geiselmann, C. Rüchardt, B. Kitschke and H. Lindner, Chem. Ber., 1980, 113, 3441.
- 29 W. N. Hubbard, D. W. Scott and G. Waddington, Experimental Thermochemistry, ed. F. D. Rossini, Interscience, New York, 1956, pp. 75-127
- 30 J. B. Pedley, R. D. Naylor and S. P. Kirby, Thermochemical Data of Organic Compounds, Chapman and Hall, London, 2nd edn., 1986
- S. P. Verevkin, Thermochim. Acta, 1999, 326, 17. 31
- R. C. Reid, J. M. Prausnitz and T. K. Sherwood, The Properties of 32 Gases and Liquids, 3rd edn., McGraw-Hill, New York, 1977,
- p. 249.S. W. Benson, *Thermochemical Kinetics*, Wiley, New York, 1976, 33 p. 274.
- N. Cohen, J. Phys. Chem. Ref. Data, 1996, 25, 1411. 34
- S. P. Verevkin, J. Chem. Thermodyn., 1998, 30, 1029 35
- G. H. Penner, T. Schaefer, R. Sebastia and S. Wolfe, *Can. J. Chem.*, 1987, **65**, 1845. 36
- 37 D. A. Pratt, J. S. Wright and K. U. Ingold, J. Am. Chem. Soc., 1999, 121, 4877.
- 38 G. A. DiLabio and D. A. Pratt, J. Phys. Chem. A, 2000, 104, 1938.
- 39 S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, J. Phys. Chem. Ref. Data, 1988, 17(Suppl. 1).
- A. A. Zavitsas, J. Phys. Chem., 1987, 91, 5573. 40
- C. P. Andreiux, A. Le Gorande and J.-M. Saveant, J. Am. Chem. 41 Soc., 1992, 114, 6892.
- 42 L. J. J. Laarhoven, J. P. G. Born, L. W. C. E. Arends and P. Mulder, J. Chem. Soc., Perkin Trans. 2, 1997, 2307
- 43 H. Hippler and J. Troe, J. Phys. Chem., 1990, 94, 3803
- X. Ma and H. H. Schobert, J. Phys. Chem. A, 2000, 104, 1064.
- D. D. M. Wayner and D. Griller, Advances in Free Radical Chem-45 istry, 1990, 1, 159-192.
- V. Pacakova and K. Feltl, Chromatographic Retention Indices; An 46 Aid to the Identification of Organic Compounds, Ellis Horwood, London, 1992.
- 47 E. M. Arnett and N. J. Pienta, J. Am. Chem. Soc., 1980, 102, 3329.
- 48 H. Y. Afeefy, J. F. Liebman and S. E. Stein, Neutral Thermochemical Data in NIST Chemistry WebBook, NIST Standard Reference Database Number 69, ed. P. J. Linstrom and W. G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, July 2001 (http://webbook.nist.gov).
- 49 S. W. Slayden, J. F. Liebman and W. G. Mallard, in The chemistry of halides, pseudo-halides and azides, ed. S. Patai and Z. Rappoport, Wiley, 1995, Supplement D2, pp. 361-402.