Substituent effects on the benzylic bond dissociation enthalpy in benzyl bromides (C–Br) and *tert*-butylbenzenes (C–CH$_3$): a gas phase thermolysis and liquid phase photoacoustic study

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The bond dissociation enthalpies in a number of substituted benzyl bromides have been studied in the gas phase, using the toluene carrier technique, and in solution with photoacoustic calorimetry. Gas phase thermolysis with unsubstituted benzyl bromide gives an absolute C–Br bond dissociation enthalpy (E_d) at 298 K of 255 ± 4 kJ mol^{-1}. Competition experiments in the gas phase reveal no substituent effect on the value of E_d(C–Br). Gas phase thermolysis with substituted *tert*-butylbenzenes also shows no effect on the C–CH$_3$ bond dissociation enthalpy for *p*-CN, *p*-OH and *p*-Bu^t substituents, with a E_d(C–CH$_3$) value at 298 K of 299 ± 2 kJ mol^{-1}. In solution, photoacoustic experiments yield no detectable substituent effect for *p*-CN, *p*-Bu^t and *m*-CF$_3$ substitution of the benzyl bromide, in contrast with other reports. With photoacoustic calorimetry a bond dissociation enthalpy of 254 ± 4 kJ mol^{-1} has been found for all benzyl bromides studied. A rationale for the absence of a substituent effect on the benzylic bond dissociation enthalpy is provided.

Introduction

The effect that substituents have on the phenolic or benzylic homolytic bond dissociation enthalpy has been a subject of study for many years. A profound substituent effect has been observed in phenols[1] with a difference of *ca.* 42 kJ mol^{-1} between *p*-OH and *p*-CN, as opposed to only a very small variation in toluenes.[2] A substantial influence (25 kJ mol^{-1} between *p*-OH and *p*-CN) has been reported on the O–CH$_3$ bond dissociation enthalpy in anisoles.[3]

In recent years discussion has focussed on the origin of this phenomenon. Substituents may impose their (de-)stabilizing influence predominantly on the closed shell compound or mainly on the radical that is formed. Bordwell *et al.*[4] proposed an additional dependency on the polarity of the bond that is broken. In that respect, it seems obvious that a substituent effect on the value of E_d(O–H) in phenols and on the E_d(C–Br) value in benzyl bromides should be different, since in the latter compounds the bond to be broken possesses opposite polarity. In the early 1950s Swarc and co-workers[5] showed, on the basis of the unimolecular decomposition rates in the gas phase, that there is no explicit substituent effect on the C–Br bond dissociation enthalpy in benzyl bromides. However, evidence in favour of a substituent effect has been published more recently.[6] A number of substituted benzyl bromides were studied in the liquid phase using photoacoustic calorimetry. This study has produced ΔE_d(C–Br) values with *ca.* 21 kJ mol^{-1} between *p*-CN- and *p*-H-benzyl bromide, with the weakest bond in the *p*-CN derivative, which is opposite to that in phenols. In another liquid phase study, using an electrochemical method,[7] a difference of −14 kJ mol^{-1} has been reported. Hence, there appears to be a discrepancy between substituent effects in benzyl bromides in the gas phase and in solution. Interestingly, no experimentally determined value for the C–Br bond dissociation enthalpy in benzyl bromide is available in the recent literature.

In order to compare solution and gas phase enthalpy data, the absolute bond dissociation enthalpies in *X*-benzyl bromides (*X* = *p*-H, *p*-Bu^t, *p*-CN and *m*-CF$_3$) have been determined in several solvents using photoacoustic calorimetry (PAC) and a number of substituted benzyl bromides have been studied with gas phase thermolysis. To study the effect of the polarity of the bond, the bond dissociation enthalpies in four *X*-*tert*-butylbenzenes (*X* = *p*-H, *p*-CN, *p*-Bu^t and *p*-OH) have also been determined with gas phase thermolysis.

Results

Gas phase thermolysis of (substituted) benzyl bromides and *tert*-butylbenzenes

Benzyl bromide. The thermolysis of benzyl bromide was conducted between 763 and 843 K in a large excess of *p*-fluorotoluene as a radical scavenger. The entrance gas mixture consisted of benzyl bromide (0.07%), *p*-fluorotoluene (1.13%) and N$_2$ (98.80%). Over this temperature region the conversion of the reactant ranged from 6 to 91% at a residence time, τ, of around 5 s. The main organic products observed were toluene, *p*,*p*′-difluorobibenzyl, together with minor amounts of *p*-fluorobibenzyl, *p*,*p*′-difluorostilbene and *p*-fluorostilbene, which can be rationalized by reactions (1)–(6).

Upon cleavage of the C–Br bond [reaction (1)] both the

$$\mathrm{PhCH_2Br} \longrightarrow \mathrm{PhCH_2^{\bullet}} + \mathrm{Br^{\bullet}} \qquad (1)$$

benzyl radical and bromine atom abstract a benzylic hydrogen from the scavenger [reactions (2) and (3)]. The *p*-fluorobenzyl

$$\mathrm{PhCH_2^{\bullet}} + p\text{-}\mathrm{F{-}C_6H_4CH_3} \longrightarrow \mathrm{PhCH_3} + p\text{-}\mathrm{F{-}C_6H_4CH_2^{\bullet}} \qquad (2)$$

$$\mathrm{Br^{\bullet}} + p\text{-}\mathrm{F{-}C_6H_4CH_3} \longrightarrow \mathrm{HBr} + p\text{-}\mathrm{F{-}C_6H_4CH_2^{\bullet}} \qquad (3)$$

radicals mainly recombine to form *p*,*p*′-difluorobibenzyl [reaction (4)]. At higher temperatures reaction (4) becomes

$$2\,p\text{-}\mathrm{F{-}C_6H_4CH_2^{\bullet}} \longrightarrow (p\text{-}\mathrm{F{-}C_6H_4CH_2})_2 \qquad (4)$$

reversible and the concentration of the *p*-fluorobenzyl radicals increases. Combination with the unsubstituted benzyl radical

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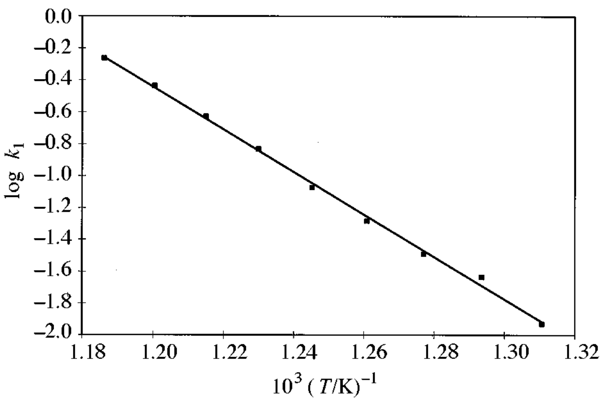

Fig. 1 Arrhenius plot for the thermolysis of benzyl bromide: $PhCH_2Br \rightarrow PhCH_2^{\bullet} + Br^{\bullet}$, $\log(k_1/s^{-1}) = 15.5\ (\pm 0.1) - 253\ (\pm 4)\ \text{kJ mol}^{-1}/2.303RT$

will then gain in importance [reaction (5)]. Stilbenes are likely

$$p\text{-F-}C_6H_4CH_2^{\bullet} + PhCH_2^{\bullet} \longrightarrow p\text{-F-}C_6H_4CH_2CH_2Ph \qquad (5)$$

to be produced from bibenzyls through benzyl mediated hydrogen abstraction and disproportionation, since under these conditions the equilibrium concentration of $p\text{-F-}C_6H_4CH_2^{\bullet}$ is relatively high (*ca.* 10^{-8} M)[8] [reaction (6)]. An induced decom-

$$(p\text{-F-}C_6H_4CH_2)_2 \xrightarrow{-H^{\bullet}} p\text{-F-}C_6H_4CH(^{\bullet})CH_2C_6H_4\text{-F-}p \xrightarrow{-H^{\bullet}} (p\text{-F-}C_6H_4CH)_2 \qquad (6)$$

position pathway [reaction (7)] for benzyl bromide, initiated by $p\text{-F-}C_6H_4CH_2^{\bullet}$, is not expected to play a significant role in view of the large excess of p-F–toluene.

$$p\text{-F-}C_6H_4CH_2^{\bullet} + PhCH_2Br \rightleftharpoons p\text{-F-}C_6H_4CH_3 + PhCH(^{\bullet})Br \qquad (7)$$

The first order rate constants were calculated according to $k_1 = -(1/\tau)\ln([PhCH_2Br]_{out}/[PhCH_2Br]_{in})$. Below 50% conversion of the reactant, k_1 was derived from product formation (*i.e.* $[PhCH_2Br]_{out} = [PhCH_2Br]_{in} - [\text{toluene}]_{out} - [p\text{-fluorobibenzyl}]_{out} - [p\text{-fluorostilbene}]_{out}$). In Fig. 1, the Arrhenius line obeying $\log k_1/s^{-1} = 15.5\ (\pm 0.1) - 253\ (\pm 4)\ \text{kJ mol}^{-1}/2.303RT$ ($r^2 = 0.998$) is plotted. The pre-exponential factor is clearly indicative of a purely homogeneous gas phase reaction.

The activation energy for a homolytic bond fission is directly related to the reaction enthalpy provided that the reverse reaction (recombination of two radicals) has no activation energy [eqn. (8)]. According to eqn. (8), at the median reaction tem-

$$\Delta_r H_T = E_a + RT_m \qquad (8)$$

perature, T_m, of 800 K, $\Delta_1 H$ is 260 kJ mol^{-1}. After $\Delta_r C_p$ correction ($\Delta_1 C_{p,(800-298)} = 9$ J mol^{-1} K^{-1}),[9] E_d(C–Br) is 255 ± 4 kJ mol^{-1} at 298 K. Using this bond dissociation enthalpy, with $\Delta_f H_{298}(PhCH_2Br) = 67$ kJ mol^{-1}[10] and $\Delta_f H_{298}(Br^{\bullet}) = 112$ kJ mol^{-1},[10] a value for $\Delta_f H_{298}(PhCH_2^{\bullet})$ of 210 kJ mol^{-1} and a $E_d(PhCH_2\text{–}H)$ of 378 kJ mol^{-1} are obtained, in good agreement with the current literature values[11] of 207 ± 4 and 370 ± 6 kJ mol^{-1} respectively.‡

Substituted benzyl bromides. To explore a large range of substituted benzyl bromides, competition experiments were conducted with various mixtures of p-H-, p-CN-, p-CF$_3$-, m-CF$_3$-, p-Bu^t-, p-Br- and p-MeO-benzyl bromide (each *ca.* 1%) dissolved in p-fluorotoluene or cumene. From these experiments, conversions were calculated on the basis of GC peak areas relative to an internal standard (o-dichlorobenzene for low-boiling, and o-dicyanobenzene or α-bromonaphthalene for high-boiling compounds).

Table 1 Ranges of k_{rel} for competitive thermolysis of (substituted) benzyl bromides[a]

	relative to	
$X\text{–}C_6H_4CH_2Br$	p-CN	p-CF$_3$
p-H	0.65→0.70	0.88→0.96
p-CF$_3$	0.67→0.62	
p-Bu^t	0.80→0.75	
p-Br	0.93→0.82	
m-CF$_3$		0.95→0.82

[a] Temperature range: 750–850 K; Conversion range: 15–95%, based on internal standards.

No attempts were made to derive the Arrhenius parameters for each individual reactant, due to a parabolic temperature profile along the axis of the reactor employed in this case. However, since the experimental conditions are the same for a particular mixture, relative rates are believed to be reliable. Although some soot formation is always observed in this type of toluene carrier experiment, the reactant based overall carbon balances were >90% and high yields of the respective toluenes were found. p-Methoxybenzyl bromide proved to be already unstable during synthesis (see Experimental section) and thermolysis of this compound led to unexpectedly high conversions at low temperatures, and low yields of p-methoxytoluene. The compound seems to be very sensitive to wall mediated degradation. The substituent effect in p-methoxybenzyl bromide could therefore not be determined.

With the relative rate constants (Table 1), the differences in activation energies, and hence the differences in bond dissociation enthalpies for C–Br can be obtained when it is accepted that the pre-exponential factors are identical. This assumption can be rationalized by considering that the entropy of activation associated with any homolytic bond cleavage process is only *ca.* 30% of the overall reaction entropy. Small changes in $\Delta_r S$ due to conformational change (freezing of the substituent's free rotation due to interaction with the radical center), for example, will not cause any significant change in the value of log A for the individual benzyl bromides. The absolute values of k_{rel} and the absence of a clear temperature dependence point to small differences in activation energy. For instance, a difference of 4 kJ mol^{-1} in E_a for the C–Br bond homolysis would produce values for k_{rel} at 750 and 850 K of 0.51 and 0.55, respectively. With a difference in bond dissociation enthalpy of 21 kJ mol^{-1} between p-H- and p-CN-benzyl bromide, as reported earlier,[6] k_{rel} would be expected to vary between 0.03 and 0.05, while a mean value of 0.67 was found in the experiments (Table 1). The experimental data from the present study therefore indicate that variation in the value of E_d(C–Br) of the benzyl bromides studied is less than 4 kJ mol^{-1}.

***tert*-Butylbenzenes.** Four *tert*-butylbenzenes were thermolized individually between 857 and 955 K. The entrance gas mixture consisted of (0.02%) p-X-*tert*-butylbenzene (X = H, Bu^t, CN, OH), (2.38%) p-fluorotoluene and (97.60%) N$_2$. Over this temperature range, the conversion of the reactant ranged from 5 to 96% at a residence time of *ca.* 6 s. Besides those originating from the radical scavenger, the main products were α-methylstyrene and styrene. After fission of the carbon–carbon bond [reaction (9)], the cumyl radical can lose a

$$p\text{-X-}C_6H_4C(CH_3)_3 \longrightarrow p\text{-X-}C_6H_4C(^{\bullet})(CH_3)_2 + CH_3^{\bullet} \qquad (9)$$

hydrogen atom (*via* a unimolecular process or by disproportionation) to yield α-methylstyrene [reaction (10)].

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‡ Another value for the heat of formation of benzyl bromide is 63.3 kJ mol^{-1}.[12] Using this value renders even more agreement. The value of 67 kJ mol^{-1} is based on an improved enthalpy of vaporization[13] applied in the NIST database.[10]

Table 2 Arrhenius parameters and bond dissociation enthalpies at 298 K for (substituted) *tert*-butylbenzenes and benzyl bromide

$X–C_6H_4C(CH_3)_3$	$\log(A/s^{-1})$	E_a/kJ mol^{-1}	$E_d^{298\,a}$/kJ mol^{-1}
p-H	15.9 ± 0.1	292 ± 2	301 ± 2
p-CN	15.9 ± 0.1	289 ± 2	298 ± 2
p-Bu^t	16.1 ± 0.1	290 ± 2	299 ± 2
p-OH	15.9 ± 0.1	288 ± 2	297 ± 2
$PhCH_2Br$	15.5 ± 0.1	253 ± 4	255 ± 4

[a] $E_d^{298} = E_a + RT_m - \Delta_r C_{p,(T_{m-298})}$; $T_m = 900$ K (Bu^t-benzenes), $\Delta_9 C_{p,(900-298)} = -3$ J mol^{-1} K^{-1} [10]; $T_m = 800$ K (benzyl bromides), $\Delta_1 C_{p,(800-298)} = 9$ J mol^{-1} K^{-1} [9].

$$p\text{-X–C}_6\text{H}_4\text{C}(^\bullet)(\text{CH}_3)_2 \longrightarrow p\text{-X–C}_6\text{H}_4\text{C}(\text{CH}_3)(\text{CH}_2) + \text{H}^\bullet \quad (10)$$

Throughout the whole temperature region the formation of styrene was observed. The ratio between α-methylstyrene and styrene varied with the degree of conversion (or temperature) but was independent of the type of reactant used. Typically, this ratio ranged from 12.4 to 2.5 (at 5 and 95% conversion, respectively). The formation of styrene cannot be readily rationalized since it requires a formal 1,2-hydrogen shift in the cumyl radical followed by elimination of a methyl radical.

The Arrhenius parameters of the compounds investigated were derived according to the method outlined above. Linear regression yielded correlation coefficients (r^2) higher than 0.998. Table 2 shows that the activation energies and hence the values of $E_d(C–CH_3)$ for *p*-H-, *p*-Bu^t-, *p*-CN- and *p*-OH-*tert*-butylbenzenes are identical within experimental error. Moreover, it demonstrates that all log *A* factors (including a statistical factor of two for *p*-Bu^t) are, as expected, identical within experimental error. With $T_m = 900$ K and $\Delta_9 C_{p,(900-298)} = -3$ J mol^{-1} K^{-1},[10] $E_d(C–CH_3)$ in *tert*-butylbenzene is then calculated to be 301 ± 2 kJ mol^{-1} at 298 K. With this bond dissociation enthalpy and $\Delta_f H_{298}$(*tert*-butylbenzene) = −21 kJ mol^{-1},[10] and $\Delta_f H_{298}(CH_3^\bullet)$ = 146 kJ mol^{-1},[10] $\Delta_f H_{298}[PhC(^\bullet)(CH_3)_2]$ becomes 134 kJ mol^{-1}. Using $\Delta_f H_{298}[PhCH(CH_3)_2] = 4$ kJ mol^{-1},[10] yields $E_d[PhC(CH_3)_2–H] = 348$ kJ mol^{-1}, again in good agreement with the literature value.[10]

Photoacoustic calorimetry with (substituted) benzyl bromides

Unsubstituted, *p*-CN-, *p*-Bu^t-, and *m*-CF$_3$-benzyl bromide were studied in various solvents using the photoacoustic method that has been described previously.[14] The C–Br bond is broken according to reactions (11)–(13). The experimentally observed

$$\text{Bu}^t\text{O–OBu}^t \xrightarrow{h\nu} 2\,\text{Bu}^t\text{O}^\bullet \quad (11)$$

$$\text{Bu}^t\text{O}^\bullet + \text{Et}_3\text{Si–H} \longrightarrow \text{Bu}^t\text{OH} + \text{Et}_3\text{Si}^\bullet \quad (12)$$

$$\text{Et}_3\text{Si}^\bullet + \text{XC}_6\text{H}_4\text{CH}_2\text{–Br} \longrightarrow \text{Et}_3\text{Si–Br} + \text{XC}_6\text{H}_4\text{CH}_2^\bullet \quad (13)$$

reaction enthalpy in solvent (mixture), A, $\Delta_{14}H^A$, is that for the overall process [reaction (14)].

$$\text{Bu}^t\text{O–OBu}^t + 2\,\text{Et}_3\text{SiH} + 2\,\text{XC}_6\text{H}_4\text{CH}_2\text{Br} \xrightarrow{h\nu} 2\,\text{Bu}^t\text{OH} + 2\,\text{Et}_3\text{SiBr} + 2\,\text{XC}_6\text{H}_4\text{CH}_2^\bullet \quad (14)$$

The C–Br solution bond dissociation enthalpy in benzyl bromide in solvent A is calculated using eqn. (15), where the

$$E_d^A(\text{XC}_6\text{H}_4\text{CH}_2\text{Br}) = \frac{\Delta_{14}H^A}{2} + \Delta_s H^A(\text{Br}^\bullet) + 380 \quad (15)$$

value 380 accounts for the gas phase heats of formation of (in kJ mol^{-1} at 298 K): $\Delta_f H(\text{Bu}^t\text{OH}) = -313$,[10] $\Delta_f H(\text{Bu}^t\text{OOBu}^t) = -341$,[15] $\Delta_f H(\text{Et}_3\text{SiH}) = -218$,[16] $\Delta_f H(\text{Et}_3\text{SiBr}) = -344$§ and $\Delta_f H(\text{Br}^\bullet) = 112$.[10] The heat of solvation of the bromine atom, $\Delta_s H(\text{Br}^\bullet)$, is taken to be equal to the solvation energy of krypton[19] and this value is negligible in benzene (−1.7 kJ mol^{-1}).[20] Any additional interaction of the bromine atom with the solvent not accounted for will be identical for all benzyl bromides in a particular solvent.

Quantum yields for reaction (11) were calculated from (measured) viscosities of the solvent mixtures according to the relation established previously.[14] The observed reaction enthalpies, $\Delta_{14}H$, obtained and apparent solution bond dissociation enthalpies, calculated using eqn. (15) are presented in Table 3.

Since reaction (12) is rather slow ($k_{12} = 5.7 \times 10^6$ M^{-1} s^{-1})[21] a fair amount of the solvent mixture must consist of triethylsilane (TES), which was used in ratios of 1 : 1 (v/v) or higher with benzene, isooctane, ethyl acetate or tetrahydrofuran (THF). Ethyl acetate and THF were chosen since both triethyl silane and the substituted benzyl bromides are highly soluble in these solvents. We found that the solubility of *p*-CN-benzyl bromide in the benzene–TES[6] and isooctane–TES mixture proved to be too low for a proper PAC experiment. Rate constants for reaction (13) as determined with laser flash photolysis (LFP) all exceed 10^8 M^{-1} s^{-1}.[22] The benzyl bromides in the present study were used in concentrations between 0.03 and 0.05 M.

The values for $\Delta_{14}H$ for unsubstituted benzyl bromide in isooctane, benzene and triethylsilane are equal. The value found in ethyl acetate is slightly different. $\Delta_{14}H$ for *p*-H- and *p*-CN-benzyl bromide in THF is quite similar, but smaller than in other solvents due to a competitive hydrogen abstraction from THF (*vide infra*). The reaction enthalpies for the three substituted benzyl bromides in ethyl acetate are identical within the margins of error.

Gas phase E_d values in benzyl bromides derived from PAC experiments

From the apparent solution E_d values obtained with eqn. (15) the gas phase (absolute) bond dissociation enthalpy can be calculated by subtracting the solvent interactions [eqn. (16)].

$$E_d^{\text{gas}}(\text{R–X}) = E_d^A(\text{R–X}) - \frac{(\Delta\Delta_s H)_{\text{app}}}{2} \quad (16)$$

The term $(\Delta\Delta_s H)_{\text{app}}$ is the solvation correction parameter[14] which has been developed for PAC experiments and has been successfully applied for the extrapolation of the gas phase bond dissociation enthalpies in phenols,[14] tetralin[23] and THF.[23] $(\Delta\Delta_s H)_{\text{app}}$ contains the adiabatic expansion coefficient of the solvent, χ_s, the volume change for reaction (11), ΔV, and accounts for the difference in solvation enthalpies between di-*tert*-butyl peroxide and *tert*-butyl alcohol [eqn. (17)]. $(\Delta\Delta_s H)_{\text{app}}$

$$(\Delta\Delta_s H)_{\text{app}} = \Delta_s H(\text{Bu}^t\text{OH}) - \Delta_s H(\text{Bu}^t\text{OOBu}^t) + \frac{\chi_s}{\Delta V} \quad (17)$$

was found[14] for the peroxide–alcohol pair to vary from −38 kJ mol^{-1} in apolar solvents (benzene, isooctane) to −54 kJ mol^{-1} in polar solvents (ethyl acetate, acetonitrile). If a value of −38 kJ mol^{-1} is applied to the experiments with triethylsilane and the mixtures with benzene or isooctane (which seems reasonable since TES is an apolar solvent), gas phase bond dissociation enthalpies for benzyl bromide of 254, 252 and 255 kJ mol^{-1} respectively are calculated. These are within the margins of error equal to the E_d(C–Br) value obtained from the thermolysis experiments.

In principle, the difference in solvation enthalpy between triethylsilane and triethylsilyl bromide, and between benzyl

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§ $\Delta_f H(\text{Me}_3\text{SiBr}) = -293$ kJ mol^{-1}.[17] Applying additivity rules[18] for methyl by ethyl replacement yields a value of $[-293 + 3 \times (-17)] = -344$ kJ mol^{-1} for $\Delta_f H(\text{Et}_3\text{SiBr})$.

Table 3 Photoacoustic experiments with (substituted) benzyl bromides

$X–C_6H_4CH_2Br$	Solvent[a]	Ratio[b]	$\Delta_{14}H^A$/kJ mol^{-1}	No. expts.	φ[c]	E_d^A(C–Br)[d]/kJ mol^{-1}
p-H	Isooctane	1:2/1:3	−289	4	0.85/0.86	236
	Benzene	1:1	−295	8	0.84	233
	Triethylsilane	Neat	−290	1	0.86	236
	Ethyl acetate	1:2	−272	1	0.86	245
	THF	1:2	−132	1	0.85	*e*
p-CN[f]	Ethyl acetate	1:2	−299	2	0.86	232
	THF	1:2	−133	1	0.85	*e*
p-Bu^t	Ethyl acetate	1:2	−308	1	0.86	227
m-CF_3	Ethyl acetate	1:2	−299	1	0.86	232

[a] Mixtures with triethylsilane. [b] v/v ratio solvent–silane. [c] Quantum yields according to $1/(1 - \varphi) = 2.6 \times \exp(0.48/\eta)$,[14,23] viscosities, η, were measured or taken from the literature. [d] Eqn. (15), experimental error ± 4 kJ mol. [e] See text. [f] Experiments with *p*-CN-benzyl bromide were also performed in isooctane and benzene. The results from these experiments are not reliable since the benzyl bromide was too insoluble for a proper PAC experiment and have been omitted.

Table 4 Gas phase C–Br bond dissociation enthalpies in benzyl bromides at 298 K

$X–C_6H_4CH_2Br$	E_d/kJ mol^{-1}	Technique
p-H	255 ± 4	Thermolysis
p-H	254 ± 4	PAC[a]
p-CN	255 ± 4	PAC[b]
p-Bu^t	251 ± 4	PAC[b]
m-CF_3	255 ± 4	PAC[b]

[a] Average from the experiments in mixtures of isooctane and TES, benzene and TES, and in neat TES; [b] in ethyl acetate.

bromide and the benzyl radical should also be taken into account. The agreement between $\Delta_{14}H$ for benzyl bromide in TES and the mixtures with isooctane or benzene, suggests that the solvent interactions are equal. The fact that the value of −38 kJ mol^{-1} for $(\Delta\Delta_sH)_{app}$ can be applied indicates that there is no net solvation effect for triethylsilane–triethylsilyl bromide and benzyl bromide–benzyl radical, *i.e.* $\Delta\Delta_sH$ for these pairs in the solvent mixture are close to zero, or $\Delta\Delta_sH$ for both pairs are equal and opposite [eqn. (18)]. In ethyl acetate an average value

$$\Delta_sH(Et_3SiBr) - \Delta_sH(Et_3SiH) = \Delta_sH(PhCH_2Br) - \Delta_sH(PhCH_2^{\bullet}) \quad (18)$$

for $(\Delta\Delta_sH)_{app}$ of −46 kJ mol^{-1} may be adopted, accounting for the presence of an apolar co-solvent, triethylsilane. The gas phase bond dissociation enthalpy in benzyl bromide is then calculated to be 268 kJ mol^{-1}, which seems too high, compared to the results in the apolar solvents.

For *p*-CN-, *p*-Bu^t- and *m*-CF_3-benzyl bromide in ethyl acetate the gas phase E_d(C–Br) values are 255, 251 and 255 kJ mol^{-1}, respectively, and is hence independent of the substituent and almost identical to the C–Br bond dissociation enthalpy in benzyl bromide.

Competition in THF. In THF a competitive hydrogen abstraction from THF takes place causing the overall enthalpy to be lower (competition in PAC has been discussed before[23]). The observed reaction enthalpy in this solvent mixture is a linear combination of the reaction enthalpies for hydrogen abstraction by the *tert*-butoxyl radical from THF and the combined reactions (12) and (13), and is given in eqn. (19), where ξ is defined by eqn. (20).

$$\Delta_rH = \xi\Delta_rH_{THF} + (1 - \xi)\Delta_rH_{12+13} \quad (19)$$

$$\xi = \frac{k_{THF}[THF]}{k_{THF}[THF] + k_{TES}[TES]} \quad (20)$$

With the H-abstraction rate constants from THF¶ by Bu^{t}O$^\bullet$ ($k_{THF} = 4.6 \times 10^6$ M^{-1} s^{-1}) and triethylsilane[21] ($k_{TES} = 5.7 \times 10^6$ M^{-1} s^{-1}), ξ is 0.44 for a 1:2 (v/v) mixture of THF (4.1 M) and triethylsilane (4.2 M). Δ_rH_{THF} has previously been found to be 0 kJ mol^{-1}.[23] $\Delta_{14}H$, calculated from eqn. (19) in this way is −230 kJ mol^{-1}. This value is higher than that obtained from the other experiments with unsubstituted benzyl bromide (approx. −300 kJ mol^{-1}, see Table 3). The same $\Delta_{14}H$ is found with *p*-CN-benzyl bromide in the same solvent mixture. However, small adjustments in the magnitude of the rate constants involved can change the outcome of eqn. (19). A lower rate constant for abstraction from TES (3.5×10^6 M^{-1} s^{-1}) shows agreement between the reaction enthalpy calculated from eqn. (19) and the other photoacoustic experiments. Most rate constants for hydrogen abstraction by Bu^{t}O$^\bullet$ have been derived from laser flash photolysis (LFP) studies. Although absolute values determined by LFP or PAC differ, the ratio between the rate constants in this case remains virtually unchanged: $k_{THF}/k_{TES} = 1.5$ (LFP) and 1.3 (PAC). It may be that with the higher concentrations applied in PAC experiments lower (apparent) rate constants are obtained, due to bulk solvent properties (*e.g.* activities instead of concentrations).

Discussion

This study has shown the absence of a substituent effect on the benzylic bond dissociation enthalpy in benzyl bromides and *tert*-butylbenzenes in the gas phase. Also our photoacoustic calorimetry results did not reveal any substituent influence. Extrapolation of the reaction enthalpies as measured by PAC from the liquid phase to the gas phase, indicates that the intrinsic (gas phase) carbon–bromine E_d values in the substituted benzyl bromides are almost identical. The absolute value is in perfect agreement with that found by the direct thermolysis method. In particular, the difference in E_d(C–Br) between the *p*-CN and *p*-H (approximately zero) is at variance with another PAC study[6] (−21 kJ mol^{-1}) and determination using an electrochemical method[7] (−14 kJ mol^{-1}). No real explanation can be put forward for this apparent discrepancy.

Bond cleavage in benzyl bromides and *tert*-butylbenzenes produce a similar carbon centered benzylic radical, in which the substituent effects are identical. EPR studies[25] on benzylic radicals have demonstrated that the degree of delocalization of the free electron varies with the nature of the substituent and its position in the aromatic ring. According to the $\sigma_\alpha{}^{\bullet}$ scale in this EPR study, two extreme cases can be found: *p*-CN increases the delocalization while *m*-CF_3 reduces the spin density in the ring. Our data do not indicate any variation in the E_d(C–Br) values between these two benzyl bromide derivatives and hence the relation between spin density assessments and enthalpy effects may not be straightforward. As an alternative, the change in the heat of formation for the radical and the parent compound should have the same magnitude. This would imply that on substitution the increments in the heats of formation of benzyl bromides and *tert*-butylbenzenes are equal.

¶ The rate constant for H-abstraction from THF was derived from photoacoustic competition experiments in ref. 23. A rate constant from a LFP study[24] is 8.3×10^6 M^{-1} s^{-1}.

Bordwell *et al.*[4] observed a linear relation between the difference in the electronegativities of the atoms forming the bond that is cleaved and the ρ value. The latter represents the slope from a linear plot of ΔE_d and the Brown substituent constants σ^+ for a set of substituted compounds. The ρ values for phenols, anilines, anisols and thiophenols are clearly positive and range from +7 to +2. For benzyl bromides a negative value (−5) has been used in the correlation, while with the enthalpy data from our study the ρ-value for benzyl bromides appears to be close to zero.

When a heteroatom (oxygen, nitrogen or sulfur) is attached directly to the aromatic ring, the interaction of its lone pair with the ring system in the parent compound can be quite substantial. Recently[26] this has been shown for substituted anisols by means of theoretical density functional theory calculations. For *para*-donor groups the stabilization of the radical is more important while for *para*-withdrawing substituents the lone pair interaction causes an additional decrease in the heat of formation of the parent compound, resulting in an increase of the bond energy. In benzyl bromides such a substantial effect in the closed shell compound is not obvious. In the benzylic compounds, any additional interaction between, for example, the C–Br bond and the remote substituent can only occur through a partial charge on the carbon attached to the aromatic ring. The electron densities on the benzylic carbon in benzyl bromides (C–Br) and *tert*-butylbenzenes (C–C) are indeed expected to be different, but since no influence of substitution was observed for either compound, the magnitude of any (de-)stabilizing effect of a substituent can only be within our experimental error, *i.e.* less than 4 kJ mol^{-1}.

Experimental

Gas-phase thermolysis

Using *p*-fluorotoluene as a carrier, the thermolyses of benzyl bromide and (substituted) *tert*-butylbenzenes were performed in the gas phase with an on-line GC-analysis instrument. Competition experiments with several substituted benzyl bromides were performed using either *p*-fluorotoluene or cumene as a carrier in a set-up with off-line GC-analysis. Both types of apparatus and the experimental procedures have been described before.[27]

On-line analysis. The instrument with on-line analysis consisted of a heated reactor (5.2 ml quartz tube) in which a continuous stream of reactant, diluted with *p*-fluorotoluene and nitrogen was thermolyzed. The product mixture was analyzed by GC. The complete apparatus could operate automatically. Samples were taken at a reference reactor temperature of 548 K (×4) (blank run) and at the reaction temperature between 750–950 K (×6).

Off-line analysis. The experiments with the apparatus with off-line analysis consisted of competitive runs with two or more (substituted) benzyl bromides in *p*-fluorotoluene or cumene as the solvent (and carrier) together with *o*-dichlorobenzene and either *o*-dicyanobenzene or α-bromonaphthalene as internal standards. Nitrogen gas was used for vaporization and as a carrier gas.

Reactions were performed in a quartz tubular reactor of 6.3 ml, at atmospheric pressure over a temperature range of 750–850 K. Liquids were introduced into the reactor by a motorized syringe pump. Residence times were around 3 s. Every experiment included a blank run at 573 K.

Photoacoustic calorimetry

The photoacoustic apparatus and procedure has been described in detail before.[14,23] The benzyl bromide experiments were performed in a non-flow fashion, using a standard fluorescence cuvette (Hellma 221) containing solutions of di-*tert*-butyl peroxide and benzyl bromide in an appropriate solvent mixture, deoxygenated by purging with argon through a capillary. A blanket of argon was maintained above the solution during the whole experiment. The instrument was calibrated using *o*-hydroxybenzophenone in the same mixtures, but without the peroxide.

Chemicals

All chemicals, except *p*-methoxybenzyl bromide and *p*-CN-*tert*-butylbenzene, were obtained from commercial sources. For thermolysis experiments they were used as received, for photoacoustic experiments they were purified using appropriate methods such as distillation and sublimation.

The synthetic procedure for *p*-methoxybenzyl bromide as described by Offerman and Vögtle[28] based on conversion of the toluene using *N*-bromosuccinimide in methyl formate, CH_2Cl_2 or CCl_4, proved unsuccessful in our experiments, as mainly bromination of the benzene ring occurred. The compound was therefore synthesized from *p*-methoxybenzyl alcohol and PBr_3 cooled in an ice–salt bath. The reaction mixture was stirred for a few hours and at 70% conversion, as determined by GC, the reaction was stopped by adding diethyl ether and water. Allowing the reaction to proceed further led to formation of polymers. The ether layer was washed with 10% $NaHCO_3$ and water, dried over $MgSO_4$ and the ether was carefully evaporated. The benzyl bromide could then be distilled *in vacuo* (bp 115 °C, 1.5 mmHg), but was found to be unstable in concentrated form. Therefore a few ml of benzene were added to the ether solution before the ether was removed. The resulting 3% solution of *p*-MeO-benzyl bromide (of *ca.* 90% purity) in benzene was stored at +4 °C.

p-CN-*tert*-butylbenzene of 98% purity was synthesized from *p*-*tert*-butylbromobenzene following a procedure described by Friedman and Shechter[29] with an overall yield of 58%.

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