Heat of Formation of the *tert*-Butyl Radical

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Calculations using a variety of high-level theoretical procedures predict a heat of formation ($\Delta H^\circ_{f\,298}$) for the *tert*-butyl radical of 57 ± 7 kJ mol^{-1}, which is slightly higher than recent experimental recommendations (51.5 ± 1.7 and 51.8 ± 1.3 kJ mol^{-1}). The heats of formation for the *tert*-butyl cation (716 ± 10 kJ mol^{-1}) and isobutene (−14 ± 8 kJ mol^{-1}) predicted by the same theoretical methods are also slightly higher than the experimental values (711.5 ± 0.2 and −16.9 ± 0.9 kJ mol^{-1}, respectively), while the proton affinity of isobutene (802 ± 4 kJ mol^{-1}) is in very good agreement with experiment (801.7 ± 1.4 kJ mol^{-1}). On the other hand, the calculated ionization energy of the *tert*-butyl radical (6.81 ± 0.06 eV) is significantly higher than two experimental values (6.58 and 6.70 eV), suggesting that a reexamination may be desirable.

Introduction

The heat of formation ($\Delta H^\circ_{f\,298}$) of the *tert*-butyl radical has been the subject of considerable debate between proponents of “low” (approximately 38 kJ mol^{-1}) and “high” (approximately 50 kJ mol^{-1}) values.[1] The situation has been reviewed recently by Berkowitz, Ellison, and Gutman,[2] Tsang,[3] and Traeger and Kompe.[4] A value for $\Delta H^\circ_{f\,298}$ of 51.5 ± 1.7 kJ mol^{-1} was recommended by Berkowitz et al.,[2] while Tsang[3] recommended a value of 48 ± 3 kJ mol^{-1}. On the other hand, Traeger and Kompe[4] noted that these values are not consistent with their recommended value for the heat of formation of the *tert*-butyl cation (711.5 ± 0.2 kJ mol^{-1}) and reported experimental values[5,6] of the adiabatic ionization energy of the *tert*-butyl radical (6.58 ± 0.1 and 6.70 ± 0.03 eV). Even the higher of these ionization energies[6] leads to a heat of formation for the *tert*-butyl radical of 65.1 ± 2.9 kJ mol^{-1}, a significant discrepancy with the recommended values noted above. It was therefore suggested[4] that both of the experimental adiabatic ionization energies might be too low and that additional experiments were desirable to resolve the discrepancy. It can be seen that the experimental heats of formation for the *tert*-butyl radical over the past 10 years span a range of nearly 30 kJ mol^{-1}. A recent measurement[1f] gives 51.8 ± 1.3 kJ mol^{-1}.

An alternative source of reliable thermochemical data comes from high-level ab initio calculations. A number of theoretical procedures have been introduced recently[7−10] that consistently produce thermochemical data to an accuracy well within 10 kJ mol^{-1}, and these procedures are therefore potentially useful in addressing questions such as the “high” versus “low” $\Delta H^\circ_{f\,298}$ for *tert*-butyl radical or the disputed ionization energy of *tert*-butyl radical. We use a variety of such high-level calculations in the present study to examine the heat of formation of the *tert*-butyl radical and, in addition, the heats of formation of the *tert*-butyl cation and isobutene. In addition, we derive the proton affinity of isobutene and the ionization energy of the *tert*-butyl radical. In previous related work,[11] we challenged the then-accepted proton affinity of isobutene, suggesting a value of 802 kJ mol^{-1} rather than the recommended experimental value[12] of 820 kJ mol^{-1}. Subsequent experiments[13] produced proton affinity values of 802.1 ± 2.1, 802 ± 3.6, and 801.7 ± 1.4 kJ mol^{-1}, strongly supporting the theoretical challenge. We note that in a recent study of the heats of formation of 148 molecules at the G2 level,[14] a $\Delta H^\circ_{f\,298}$ value for the *tert*-butyl radical of 59.8 kJ mol^{-1} was reported without comment.

Theoretical Procedures

Ab initio molecular orbital calculations[15] were performed using the GAUSSIAN 94,[16] MOLPRO,[17] and ACESII[18] programs. Unless otherwise noted, heats of formation at 298 K were calculated using the atomization method as detailed by Nicolaides et al.,[19] but isodesmic reaction energies[15,20,21] were also employed in some cases. Scale factors for vibrational frequencies, used to obtain zero-point vibrational energies (ZPVEs) and enthalpy temperature corrections, were taken from a recent study by Scott and Radom.[22] In the calculation of the enthalpy temperature corrections, the methyl rotations for *tert*-butyl radical and *tert*-butyl cation were treated as free rotors (each contributing $RT/2$) while those for isobutene were treated as harmonic oscillators, consistent with the recommendations of East et al.[23] Total energies were obtained from several variations of the G2[7] and CBS-Q[10] composite methods.

The variants of the G2 method that we have used include G2,[7] G2(MP2),[8] G2(MP2,SVP),[9] G2-RAD,[24] and G2(MP2)-RAD.[24] The G2 method provides energies effectively at the QCISD(T)/6-311+G(3df,2p)//MP2(full)/6-31G(d) level together with zero-point vibrational energy (ZPVE) and higher-level correction (HLC) contributions. The G2(MP2) and G2(MP2,SVP) methods reduce the size of the largest calculations that are required to produce the total composite energy and thus present substantial savings in computational time over the original G2 method, generally with only a small loss in accuracy.

The RAD variations of G2 theory have been recently introduced[24] to deal better with radical systems. The additivity schemes are the same as their original counterparts but the QCISD(T) component of the energy is replaced by a CCSD(T) energy, and all correlation calculations are performed using spin-restricted open-shell wave functions. The restricted open-shell

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TABLE 1: Calculated Heats of Formation ($\Delta H^\circ_{f\ 298}$, kJ mol^{-1}), Proton Affinities (PA$_{298}$, kJ mol^{-1}), Ionization Energies (IE, 0 K, eV), Zero-Point Vibrational Energies (ZPVE, kJ mol^{-1}), and Enthalpy Temperature Corrections (ΔH_{298-0}, kJ mol^{-1})

			tert-butyl radical			*tert*-butyl cation			isobutene				
	geom[a]	freq[a]	ZPVE	ΔH_{298-0}	$\Delta H^\circ_{f\ 298}$	ZPVE	ΔH_{298-0}	$\Delta H^\circ_{f\ 298}$	ZPVE	ΔH_{298-0}	$\Delta H^\circ_{f\ 298}$	PA$_{298}$	IE
G2	MP2	HF[b]	293.6	17.9	58.3	293.4	17.6	712.6	271.2	16.8	−14.2	803.3	6.78
	MP2	HF[c]	300.3	18.0	58.4	300.1	17.6	712.6	277.4	16.8	−14.6	802.8	6.78
	MP2	MP2[d]	299.1	17.3	63.3	296.5	16.9	715.1	274.0	16.2	−11.9	803.0	6.76
	MP2	MP2[e]	306.5	17.3	64.0	303.9	16.9	715.7	280.8	16.2	−11.8	802.5	6.75
	MP2	B3LYP[f]	296.0	17.6	60.4	295.5	17.1	714.2	273.9	16.4	−11.8	803.9	6.78
	MP2	B3LYP[g]	301.9	17.6	59.6	301.4	17.1	713.4	279.3	16.4	−13.1	803.5	6.78
G2(MP2)	MP2	HF[b]	293.6	17.9	63.8	293.4	17.6	718.0	271.2	16.8	−9.8	802.1	6.78
	MP2	HF[c]	300.3	18.0	63.9	300.1	17.6	718.1	277.4	16.8	−10.3	801.6	6.78
	MP2	MP2[d]	299.1	17.3	68.7	296.5	16.9	720.6	274.0	16.2	−7.6	801.9	6.76
	MP2	MP2[e]	306.5	17.3	69.4	303.9	16.9	721.2	280.8	16.2	−7.5	801.3	6.76
	MP2	B3LYP[f]	296.0	17.6	65.9	295.5	17.1	719.7	273.9	16.4	−7.5	802.8	6.78
	MP2	B3LYP[g]	301.9	17.6	65.1	301.4	17.1	718.9	279.3	16.4	−8.8	802.4	6.78
G2(MP2,SVP)	MP2	HF[b]	293.6	17.9	57.4	293.4	17.6	709.2	271.2	16.8	−20.4	800.4	6.76
G2-RAD	QCISD	B3LYP[g]	301.9	17.6	61.3	301.4	17.1	715.2	279.3	16.4	−12.0	802.5	6.78
	B3LYP	B3LYP[g]	301.9	17.6	61.8	301.4	17.1	715.6	279.3	16.4	−11.9	802.9	6.78
G2(MP2)-RAD	QCISD	B3LYP[g]	301.9	17.6	67.1	301.4	17.1	721.4	279.3	16.4	−6.9	801.3	6.79
	B3LYP	B3LYP[g]	301.9	17.6	67.6	301.4	17.1	721.8	279.3	16.4	−6.8	801.7	6.79
CBS-Q	MP2[h]	HF[i]	300.5	17.8	60.1	300.3	17.4	721.0	277.5	16.6	−9.1	799.9	6.85
CBS(QCISD,B3LYP)-RAD	QCISD	B3LYP[g]	301.9	17.6	62.2	301.4	17.1	723.4	279.3	16.4	−6.7	799.9	6.86
CBS(B3LYP,B3LYP)-RAD	B3LYP	B3LYP[g]	301.9	17.6	62.6	301.4	17.1	723.7	279.3	16.4	−6.8	799.5	6.86
exptl					51.8 ± 1.3[j]			711.5 ± 0.2[k]			−16.9 ± 0.9[l]	801.7[k]	6.70[m]

[a] Geometries and frequencies obtained with the 6-31G(d) basis unless otherwise stated. [b] HF/6-31G(d) frequencies scaled by 0.8929 for ZPVE and temperature corrections. Higher-level correction factor $A = 4.81$ for G2 and G2(MP2) and $A = 5.13$ for G2(MP2,SVP). [c] HF/6-31G(d) frequencies scaled by 0.9135 for ZPVE and 0.8905 for temperature corrections. Higher-level correction factor $A = 5.13$. [d] MP2/6-31G(d) frequencies scaled by 0.9427 for ZPVE and 1.0084 for temperature corrections. Higher-level correction factor $A = 4.81$. [e] MP2/6-31G(d) frequencies scaled by 0.9661 for ZPVE and 1.0084 for temperature corrections. Higher-level correction factor $A = 5.13$. [f] B3LYP/6-31G(d) frequencies scaled by 0.9614 for ZPVE and 0.9989 for temperature corrections. Higher-level correction factor $A = 4.81$. [g] B3LYP/6-31G(d) frequencies scaled by 0.9806 for ZPVE and 0.9989 for temperature corrections. Higher-level correction factor $A = 5.13$. [h] Geometries optimized with 6-31G† basis. [i] HF/6-31G† frequencies scaled by 0.91844 for ZPVE and temperature corrections. [j] Reference 1f. [k] Reference 4. [l] Reference 12. [m] Reference 6.

URCCSD(T) calculations[25] were performed using the MOLPRO program,[17] while the ACESII program[18] was used to obtain the restricted open-shell Møller−Plesset (RMP) energies.[26] Geometries and vibrational frequencies are evaluated at the QCISD/6-31G(d) or B3-LYP/6-31G(d) levels.

The CBS family of model chemistries combines an extrapolation to the complete basis set (CBS) limit with smaller basis set higher-order correlation calculations to provide accurate energies.[10] A spin-correction term is included to compensate for spin contamination in the unrestricted wave functions. The CBS-RAD method[27] differs from CBS-Q by the replacement of the quadratic configuration interaction (UQCISD(T)) single-point energy with a coupled-cluster energy (UCCSD(T)), and by the use of QCISD/6-31G(d) or B3-LYP/6-31G(d) geometries and vibrational frequencies.

For the G2 approach, we have calculated vibrational frequencies at several different levels of theory with different vibrational frequency scale factors. The scale factors fall into three groups: (i) the scale factor prescribed for the particular method (0.8929 for HF/6-31G(d) for G2 and 0.91844 for HF/6-31G† for CBS-Q), (ii) scale factors appropriate for reproducing fundamental vibrational frequencies (0.9427 for MP2/6-31G(d) and 0.9614 for B3-LYP/6-31G(d)),[22] and (iii) scale factors appropriate for reproducing ZPVEs (0.9135 for HF/6-31G(d), 0.9661 for MP2/6-31G(d), and 0.9806 for B3-LYP/6-31G(d)).[22]

The higher-level correction (HLC) is applied in G2 theory largely to account for basis set deficiencies. This correction is HLC $= -An_\beta - Bn_\alpha$, where $B = 0.19$ millihartree (mh) and n_α and n_β are the number of alpha and beta valence electrons, respectively. The values of A have been previously derived by minimizing (according to various measures) the deviation from experiment for the calculated atomization energies of 55 molecules having well-established experimental values, and they depend on the particular variation of G2 theory employed.[28] A value of $A = 4.81$ mh is used in the standard G2 and G2(MP2) approaches,[7,8] while $A = 5.13$ mh is used for G2(MP2,SVP).[9] In a variation of G2 theory where MP2/6-31G(d) frequencies (scaled to reproduce ZPVEs) are used in the calculation of ZPVEs in place of the standard HF/6-31G(d) frequencies (scaled to reproduce fundamental vibrational frequencies), a different value of $A = 5.13$ mh was obtained.[28] Thus, the function of the HLC is not only to correct for basis set deficiencies but also to account for other deficiencies, including errors in the evaluation of the ZPVE. Throughout the G2 and G2(MP2) calculations of the present study, we have used $A = 4.81$ mh when a vibrational frequency scale factor is applied to the vibrational frequencies and $A = 5.13$ mh when a ZPVE scale factor is used.

Results

Heats of formation calculated using the atomization method for the *tert*-butyl radical, *tert*-butyl cation, and isobutene, obtained at several different levels of theory, are presented in Table 1, together with the proton affinity of isobutene and the ionization energy of the *tert*-butyl radical. Also included in Table 1 are the calculated ZPVEs and thermal corrections. Cartesian coordinates of the optimized structures are provided as Supporting Information.[29]

Inspection of the first block of G2 data in Table 1 shows differences between the various G2 heats of formation characteristic of the method used to calculate the vibrational frequencies. Thus, for example, the G2 heat of formation for the *tert*-butyl radical is approximately 58 kJ mol^{-1} when HF frequencies are used, 64 kJ mol^{-1} when MP2 frequencies are used, and 60 kJ mol^{-1} when B3-LYP frequencies are used. However, the choice of vibrational frequency scale factor (i.e., one that is

TABLE 2: Calculated Reaction Enthalpies (ΔH_{298}) and Heats of Formation ($\Delta H^\circ_{f\ 298}$, kJ mol^{-1})

					$\Delta H^\circ_{f\ 298}$	
	geom[a]	freq[a]	$\Delta H_{298}(1)^j$	$\Delta H_{298}(2)^k$	*tert*-butyl radical	*tert*-butyl cation
G2	MP2	HF[b]	−30.6	−319.0	57.1	716.6
	MP2	HF[c]	−30.5	−318.6	57.2	717.0
	MP2	MP2[d]	−32.7	−320.6	54.9	715.1
	MP2	MP2[e]	−30.8	−320.2	56.9	715.5
	MP2	B3LYP[f]	−32.2	−319.7	55.5	716.0
	MP2	B3LYP[g]	−32.1	−319.2	55.5	716.4
G2(MP2,SVP)	MP2	HF[b]	−30.0	−319.7	57.7	716.0
G2-RAD	B3LYP	B3LYP[g]	−31.1	−318.5	56.6	717.2
CBS-Q	MP2[h]	HF[i]	−31.7	−317.4	55.9	718.2
CBS(B3LYP,B3LYP)-RAD	B3LYP	B3LYP[g]	−33.1	−317.2	54.5	718.4

[a−i] See footnotes for Table 1. [j] Reaction enthalpy for isodesmic reaction 1. [k] Reaction enthalpy for isodesmic reaction 2.

optimal for frequencies or one that is optimal for ZPVEs) in the ZPVE evaluations within the G2 calculations does not appear to strongly affect the resultant heat of formation, provided that the appropriate HLC is also used. The thermal corrections are not sensitive to their method of calculation and vary by less than 1 kJ mol^{-1}.

Curtiss et al.[14] have recently shown that the G2 method provides good values for the heats of formation for hydrocarbons, with a mean absolute deviation from experiment of 5.4 kJ mol^{-1}. The G2(MP2,SVP) method appears to perform particularly well for hydrocarbons (mean absolute deviation of 3.2 kJ mol^{-1}), while G2(MP2) seems to overestimate heats of formation for such species (mean absolute deviation 7.7 kJ mol^{-1}). The present results are consistent with these observations, in particular the G2(MP2) and G2(MP2)-RAD heats of formation being between 4.3 and 6.2 kJ mol^{-1} higher than their G2 counterparts. These are therefore disregarded in the discussion that follows. The G2(MP2,SVP) heats of formation, on the other hand, agree well with the G2 results. The G2-RAD heats of formation are very similar to the G2 results obtained with B3-LYP vibrational frequencies. We note that there appears to be no advantage in using the more expensive QCISD geometries over B3-LYP, the resulting differences in heats of formation being less than 0.5 kJ mol^{-1}. This is also true for the CBS-RAD method: only small differences are observed between results obtained using the B3-LYP and QCISD optimized geometries. The CBS-RAD heats of formation are 2−3 kJ mol^{-1} higher than the CBS-Q results. Previous work[24] has suggested that CBS-RAD tends to give heats of formation for hydrocarbons that are slightly overestimated.

We have also obtained heats of formation for the *tert*-butyl radical and *tert*-butyl cation from the calculated enthalpies for the following isodesmic reactions:

$$\text{isobutane} + CH_3^{\bullet} \rightarrow \textit{tert}\text{-butyl radical} + CH_4 \qquad (1)$$

$$\text{isobutane} + CH_3^{+} \rightarrow \textit{tert}\text{-butyl cation} + CH_4 \qquad (2)$$

together with experimental heats of formation[31] for the remaining species. Results obtained using a selection of our best levels of theory are presented in Table 2. The heats of formation obtained in this manner show much less variation than those from the atomization method; the total range of values is less than 3.5 kJ mol^{-1} in each case.

Discussion

For the *tert*-butyl radical, our best levels of theory (G2, G2(MP2,SVP), G2-RAD and CBS-RAD) produce heats of formation from atomization energies in the range 58−64 kJ mol^{-1} (Table 1). The values obtained from isodesmic comparisons are somewhat lower at 54.5−57.7 kJ mol^{-1} (Table 2). Our best theoretical estimate, obtained as a subjective average of all these values, is 57 ± 7 kJ mol^{-1}. This supports the "high" rather than "low" experimental values from the literature. It is in fact even slightly higher than recent recommended values[1f,2,3] of 48 ± 3, 51.5 ± 1.7, and 51.8 ± 1.3 kJ mol^{-1}, although the differences are well within the combined theoretical and experimental uncertainties.

For the *tert*-butyl cation, the G2, G2(MP2,SVP), and G2-RAD heats of formation obtained using the atomization method lie in the range 709.2−715.7 kJ mol^{-1} (Table 1). The CBS-RAD values are somewhat higher at 723.4 and 723.7 kJ mol^{-1}. The values obtained using isodesmic comparisons lie in the range 715.1−718.4 kJ mol^{-1} (Table 2). Our best theoretical estimate, again the result of a subjective average, is 716 ± 10 kJ mol^{-1}. This is slightly higher than the most recent recommended value of Traeger and Kompe[4] of 711.5 ± 0.2 kJ mol^{-1}.

For isobutene, the G2, G2(MP2,SVP), and G2-RAD heats of formation lie between −11.8 and −20.4 kJ mol^{-1} (Table 1). CBS-RAD is again higher (less negative), with values of −6.7 and −6.8 kJ mol^{-1}. Our best theoretical estimate is −14 ± 8 kJ mol^{-1}. This is in good agreement with the well-established experimental value[12] of −16.9 kJ mol^{-1}.

There is a very narrow range for the predictions of the proton affinity of isobutene (Table 1). These all lie between 799.5 and 803.9 kJ mol^{-1}. Our best theoretical estimate is 802 ± 4 kJ mol^{-1}, in excellent agreement with three recent experimental values[13] of 802.1 ± 2.1, 802 ± 3.6, and 801.7 ± 1.4 kJ mol^{-1}.

The various G2 methods predict ionization energies for *tert*-butyl radical that cover a very small range, 6.75−6.78 eV (Table 1). However, in this case the CBS methods predict a somewhat larger value of 6.86 eV, which arises from the larger heats of formation for the *tert*-butyl cation. Our best theoretical estimate is 6.81 ± 0.06 eV. This is higher than either of the previous experimental estimates (6.58 and 6.70 eV),[5,6] consistent with a recent suggestion[4] that the experimental values may be too low. Using our recommended ionization energy and calculated temperature corrections, together with the experimental heat of formation for the *tert*-butyl cation, leads to a heat of formation for the *tert*-butyl radical of 55 kJ mol^{-1}, in close agreement with our best estimate.

Conclusions

The calculated heats of formation of the *tert*-butyl radical, *tert*-butyl cation, and isobutene are in good agreement with experiment, the theoretical values being 3−6 kJ mol^{-1} higher than the most recent estimates. There is very good agreement between theory and experiment for the proton affinity of isobutene. However, our calculated ionization energy for the *tert*-butyl radical supports a recent suggestion that the experimental values are probably too low.

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Supporting Information Available: Cartesian coordinates of optimized structures (3 pages). See any current masthead page for ordering and Internet access instructions.

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