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The enthalpy of formation of the pentane-2,4-dionate radical: A complete basis set approach

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Abstract

Thermochemical properties of pentane-2,4-dione (acetylacetone, Hacac) and its radical (acac) were investigated by DFT and ab initio calculations based on complete basis set (CBS) extrapolation procedures, including CBS-QB3 and a modified CBS procedure that we named CBS-QB3-tz. We provide evidence that the most stable acac radical conformer is generated by C–H bond homolysis. The enthalpy of formation of gaseous acac, $\Delta_f H^\circ$(acac,g), was estimated as −228.3 kJ/mol (CBS-QB3) and −226.7 kJ/mol (CBS-QB3-tz). Based on these results, our recommended value for $\Delta_f H^\circ$(acac,g) is -227 ± 8 kJ/mol, implying that many literature values reported for metal–acac bond dissociation enthalpies in coordination complexes should be revised.

1. Introduction

The thermochemistry of metal complexes involving the pentane-2,4-dionate (or acetylacetonate = acac) ligand has been the subject of numerous studies [1,2]. Many of these works reported not only the standard enthalpies of formation of the complexes but also the metal–acac bond dissociation enthalpies, DH°(M–acac), or mean bond dissociation enthalpies $\langle DH^\circ(\text{M–acac})\rangle$, in the gas phase (the acac ligand is bonded to the metal center by the two oxygen atoms). These quantities are related to the enthalpies of reactions (1) and (3) and are defined by Eqs. (2) and (4), respectively

$$\text{M(acac)}_n\ (\text{g}) \rightarrow \text{M(acac)}_{n-1}\ (\text{g}) + \text{acac}\ (\text{g}) \quad (1)$$

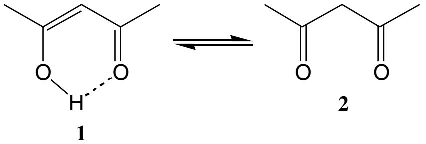
$$\Delta_r H^\circ(1) = DH^\circ(\text{M–acac}) = \Delta_f H^\circ[\text{M(acac)}_{n-1}, \text{g}] + \Delta_f H^\circ(\text{acac, g}) - \Delta_f H^\circ[\text{M(acac)}_n, \text{g}] \quad (2)$$

$$\text{M(acac)}_n(\text{g}) \rightarrow \text{M}\ (\text{g}) + n(\text{acac})\ (\text{g}) \quad (3)$$

$$\Delta_r H^\circ(3)/n = \langle DH^\circ(\text{M–acac})\rangle = \Delta_f H^\circ(\text{M, g}) + n\Delta_f H^\circ(\text{acac, g}) - \Delta_f H^\circ[\text{M(acac)}_n, \text{g}] \quad (4)$$

In both cases, the enthalpy of formation of the acac radical is required. Surprisingly, to our knowledge, this quantity has never been accurately derived. Therefore, all the literature values of metal–acac bond dissociation enthalpies rely on estimates of $\Delta_f H^\circ$(acac,g) of unknown accuracy.

The standard enthalpy of formation of liquid pentane-2,4-dione or acetylacetone (Hacac) was determined by several authors [3], but the most reliable value, -425.5 ± 1.0 kJ/mol, relies on combustion calorimetry experiments by Hacking and Pilcher [4]. Acetylacetone, which is also a model system for investigating intramolecular proton transfer in solution [5], is a mixture of two tautomers, the enol (**1**) and the keto forms (**2**). In liquid acetylacetone the enol form is the most abundant (molar fraction 0.814). In polar solvents the keto population is increased, whereas non-polar solvent favors the enol form



(5)

The enthalpies of reaction (5) in the liquid and in the gas phase, quoted by Hacking and Pilcher [4], are 11.3 ± 0.4

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and 10.0 ± 0.8 kJ/mol, respectively (the stabilization of the enol form can be attributed to the intramolecular hydrogen bond). The first of these values, together with $\Delta_f H^\circ$(Hacac,l) and the molar fractions of enol and keto tautomers in the liquid phase, leads to $\Delta_f H^\circ$(Hacac,l,enol) = −427.6 ± 1.0 kJ/mol and $\Delta_f H^\circ$(Hacac,l,keto) = −416.3 ± 1.1 kJ/mol. Finally, using the enthalpy of vaporization for the enol form recommended by Hacking and Pilcher, 43.2 ± 0.1 kJ/mol, one obtains $\Delta_f H^\circ$(Hacac,g,enol) = −384.4 ± 1.0 kJ/mol and $\Delta_f H^\circ$(Hacac,g,keto) = −374.4 ± 1.3 kJ/mol.

The standard enthalpy of formation of the acac radical can be derived either from the gas-phase O–H bond dissociation enthalpy of Hacac (enol), $DH^\circ(\text{acac–H})_{\text{enol}}$, or from the gas-phase C–H bond dissociation enthalpy of Hacac (keto), $DH^\circ(\text{acac–H})_{\text{keto}}$. Several estimates of $DH^\circ(\text{acac–H})_{\text{enol}}$ are available in the literature. However, as pointed out by Sharpe and Richardson [6], the disagreement is large: values range from 365 to 460 kJ/mol. For instance, Irving and Ribeiro da Silva assumed $DH^\circ(\text{acac–H})_{\text{enol}}$ = 418 ± 21 kJ/mol, by considering that the O–H bond dissociation enthalpy in acetylacetone should be comparable with DH°(O–H) in alcohols [7]. At the time, the 'best' values for these bond dissociation enthalpies in *n*-alkanols, were around 430 kJ/mol. Using more recent data for the alcohols, ca. 440 kJ/mol [8], the above estimate becomes $DH^\circ(\text{acac–H})_{\text{enol}}$ = 428 ± 21 kJ/mol. A significantly lower value, $DH^\circ(\text{acac–H})_{\text{enol}}$ = 365 kJ/mol, was predicted by Cavell and Pilcher [9]. It was based on an estimate for the C–H bond dissociation enthalpy for the keto tautomer, but this value was reassessed in a later publication by Cavell et al., who recommended 400 ± 20 kJ/mol [10]. The most recent estimate, 368 ± 25 kJ/mol, relies on the acidity of acetylacetone, the electron affinity of acac radical, and the ionization energy of the hydrogen atom [6]. Given the uncertainties affecting all the above estimates and the importance of an accurate value for DH°(acac–H), we decided to carry out a theoretical investigation based on high-level computational chemistry, with emphasis on extrapolation to complete basis set procedures, to settle this matter. All the present calculations for thermochemical properties include thermal corrections to 298 K.

2. Theoretical procedures

The adequacy of a given theoretical approach for predicting accurate homolytic bond dissociation enthalpies depends on the reliable estimation of geometries, vibrational frequencies, and total energies for both closed and open shell species. Given the slow convergence of ab initio energies with the basis set size, extrapolation procedures to infinite basis set are very important for accurate energy predictions. For this purpose, several composite procedures as, for example, the CBS-QB3 method [11] were proposed.

Usually, extrapolation procedures are focused on the prediction of the electronic energy and are based on a series of single-point energy calculations by using a structure optimized with a finite basis set. The structure of small molecules can be accurately predicted by high level ab initio methods. However, for large molecules, geometry optimization at a correlated level and with a large basis set becomes unaffordable for many cases of interest. Thus, it is important to propose a procedure that predicts reliable structures, which can be taken as a starting point for energy extrapolation methods. With exception of a few DFT methods, as for example the B3P86 hybrid functional [12,13], previous studies indicate that, in general, density functional theory (DFT) underestimates homolytic bond dissociation enthalpies [14]. On the other hand, it is generally accepted that DFT is adequate for predicting the structure of both closed shell molecules and radical species [15]. It has been verified, for a series of open shell molecules, that by combining the hybrid B3LYP functional [12,16], with the correlation consistent cc-pVTZ [17] basis set, the predicted (B3LYP/cc-pVTZ) geometries are in very good agreement with experiment. In addition, deviations from experiment are similar, or even smaller, than those corresponding to CCSD/cc-pVTZ optimizations [15]. Therefore, we adopted the following procedure. First, B3LYP/cc-pVTZ optimizations were carried out with a very tight convergence criteria and harmonic frequencies (scaled by 0.985 as in the W1 method [18]) were determined with a ultrafine grid. Then, B3P86/cc-pVXZ//B3LYP/cc-pVTZ (X = T,Q,5) single-point energies were calculated and extrapolation to complete basis carried out by fitting the energy to the power law expression $E_X = E_\infty + A_3X^{-3} + A_5X^{-5}$ [14]. Thermal corrections were estimated from B3LYP/cc-pVTZ optimizations. The usual rigid-rotor/harmonic oscillator model was used for estimating thermal corrections. Since reaction enthalpies involve differences between thermal corrections, it is expected that this approach is adequate for the present purposes.

By using B3LYP/cc-pVTZ structures, complete basis set (CBS) energies were also determined through a composite procedure based on the CBS-QB3 method [11] with the minimum population localization scheme [11]. The only difference of the present approach, in comparison with the standard CBS-QB3 procedure, is that the reference geometries and frequency calculations are based on B3LYP/cc-pVTZ optimizations, whereas the standard method relies on B3LYP/6-311G(d,p) optimized structures and frequencies. We designate the present procedure as CBS-QB3-tz. For comparison, calculations with the CBS-QB3 method are also reported. All the calculations were performed with the GAUSSIAN 03 package of programs [19].

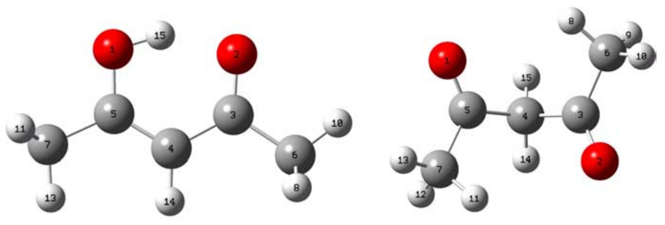
3. Results and discussion

3.1. Structural properties

The molecular structure of Hacac has been the subject of several experimental [20–26] and theoretical studies [23,24,27]. Early studies considered a planar, symmetric

C_{2v} [20,21] or an asymmetric C_s structure [20]. In either case, a C_{3v} local symmetry was postulated for the methyl groups. Consequently, the question of the relative orientation and geometrical deformation of these groups was not fully addressed. Sliznev et al. [27] studied the Hartree–Fock potential energy surface (PES) for the internal rotation of the methyl groups in Hacac (enol) and one PES minimum, corresponding to only one C_s structure, was found. The C_s optimized geometry of the enol tautomer predicted by the present calculations is in keeping with experimental data and previous theoretical studies. Our theoretical results for the structure of Hacac (enol (**1**) and keto (**2**) tautomers) are shown in Fig. 1 and in Table 1. In general, a good agreement with experimental information can be observed [22–26], although some discrepancies relative to recent experimental information based on thermally averaged structures [23,24] can be observed. The agreement between the enol/keto geometries and experimental information [22–26] strongly indicates that the present reported structures correspond to global minima.

Experimental information on the structure of the acac radical is apparently not available, although the structures of some conformers determined at the HF/6-31+G(d) level have been reported by Irikura [28]. The structures of seven conformers (**3a**–**g**) of the acac radical are shown in Fig. 2 and structural data are reported in Table 1. Although energy barriers between the conformers are of great interest, here we will focus on the enthalpies relative to the most stable structure of the acac radical (**3a**), which can be generated by the C–H bond homolysis of the methyl rotor adjacent to the OH group in the parent enol (**1**) tautomer. A second conformer **3c** (23.9 kJ/mol above **3a**) is produced by the C–H bond homolysis of the methyl group adjacent to the carbonyl. The most stable radical structure associated with the O–H bond homolysis (**3b**) is 15.2 kJ/mol above **3a**. This conformer can also be generated from the C–H bond homolysis of the Hacac keto (**2**) tautomer. The O–H bond homolysis of the enol (**1**) form also generates conformers **3e** and **3g**, which are 35.8 and 63.5 kJ/mol above **3a**, respectively.



1 (C_s)
[0.0]

2 (C_2)
[13.7]

Fig. 1. Structures of the enol (**1**) and the keto (**2**) forms of Hacac optimized at the B3LYP/cc-pVTZ level. The Hacac (enol) → (keto) tautomerisation enthalpy (in brackets) was calculated at the CBS-QB3-tz level.

3.2. Thermochemical properties

Total enthalpies and thermochemical properties at 298 K are reported in Table 2. The enthalpy of reaction (5), which corresponds to the Hacac (enol) → (keto) tautomerisation by hydrogen shift ranges from 33.5 kJ/ mol (B3P86 complete basis-set extrapolated energies) to 14 kJ/mol (CBS methods), the latter being in good agreement with the experimental value obtained by Hacking and Pilcher (10.0 ± 0.8 kJ/mol) [4].

The theoretical bond dissociation enthalpies DH°(acac–H) can be determined for both the enol and the keto tautomers of Hacac through the usual procedures: the acac–H bond homolysis (reaction (6)) or an isodesmic and/or isogyric process involving a suitable radical (R) (reaction (7))

$$\text{Hacac (g)} \rightarrow \text{acac (g)} + \text{H (g)} \tag{6}$$

$$\text{Hacac (g)} + \text{R (g)} \rightarrow \text{acac (g)} + \text{RH (g)} \tag{7}$$

For both methods, the reaction enthalpies were computed by using the sum of the electronic energy and translational, rotational, and vibrational contributions to the enthalpy of the species involved. In the case of the isodesmic and/or isogyric reaction method, the reaction enthalpy is equal to the difference between the acac–H and R–H bond dissociation enthalpies and DH°(acac–H) can be derived by using an experimental value for DH°(R–H) [8,29]. The results, obtained at the different theory levels, are displayed in Table 2.

To calculate the values of the acac–H bond dissociation enthalpies, the most stable conformer (**3a**) was taken as reference. Therefore, as the homolytic cleavage of the Hacac (enol) and Hacac (keto) are anchored on the *same* radical species (conformer **3a**), a single value of the standard enthalpy of formation of the radical should be obtained. In other words, $DH^\circ(\text{acac–H})_{\text{enol}}$ and $DH^\circ(\text{acac–H})_{\text{keto}}$ must be thermodynamically consistent. Hence, the final selection has to be made on the basis of $\Delta_f H^\circ$(acac,g). Each value for this quantity, displayed in Table 2, was derived by using the computed $DH^\circ(\text{acac–H})_{\text{enol}}$ or $DH^\circ(\text{acac–H})_{\text{keto}}$, together with the experimental gas-phase enthalpies of formation of Hacac (enol) and Hacac (keto) (−384.4 ± 1.0 and −374.4 ± 1.3 kJ/mol, respectively) [4], and $\Delta_f H^\circ(\text{H,g}) = 217.998 \pm 0.006$ kJ/mol [30]. The averages of the seven values computed with the CBS-QB3 and CBS-QB3-tz methods (in bold in Table 2) are −228.3 kJ/mol (CBS-QB3) and −226.7 kJ/mol (CBS-QB3-tz). We therefore recommend −227 kJ/mol for the enthalpy of formation of acac, to which a conservative estimate of the error (8 kJ/mol) is assigned.

It is also interesting to note that the thermodynamic consistency of the results obtained from each theory level can be assessed by the difference $\Delta\Delta_f H^\circ(\text{acac,g}) = \Delta_f H^\circ(\text{acac,g})_{\text{enol}} - \Delta_f H^\circ(\text{acac,g})_{\text{keto}}$, where the enthalpies of formation of the radical are calculated from the O–H or C–H bond dissociation enthalpy (see above). Obviously, the dif-

Table 1
Structural data of the enol (**1**) and keto (**2**) Hacac isomers and the radical structures (**3a**–**g**)

	1	Exp.[a]	Exp.[b]	**2**	**3a**	**3b**	**3c**	**3d**	**3e**	**3f**	**3g**
	C_s	C_s	C_1	C_2	C_s	C_s	C_s	C_2	C_2	C_1	C_{2v}
d(O1–O2)	2.533	2.512 ± 0.08; 2.535[c]; 2.547[d]	$\sim$2.592	4.012[e]	2.587	4.215	2.507	4.574	2.927	4.116	2.196
d(O1–H15)	1.006	1.049 ± 0.015			0.991		1.016				
d(O2–C3)	1.244	1.243 ± 0.002	1.262 ± 0.005	1.208	1.243	1.226	1.263	1.228	1.219	1.208	1.256
d(O1–C5)	1.323	1.319 ± 0.003	1.321 ± 0.021	1.208	1.340	1.228	1.320	1.228	1.219	1.208	1.256
d(C4–C3)	1.440	1.430 ± 0.008	1.443 ± 0.019	1.533	1.438	1.457	1.444	1.459	1.466	1.533	1.399
d(C4–C5)	1.367	1.382 ± 0.007	1.359 ± 0.034	1.533	1.403	1.463	1.370	1.459	1.466	1.533	1.399
d(C5–C7)	1.492	1.493 ± 0.009		1.507	1.389	1.506	1.491	1.512	1.517	1.430	1.513
d(C3–C6)	1.509	1.522 ± 0.007		1.507	1.510	1.514	1.434	1.512	1.517	1.507	1.513
d(C4–H14)	1.079	1.099 ± 0.003		1.088	1.080	1.083	1.078	1.083	1.085	1.088	1.076
α(O1–H15–O2)	149.6	137 ± 7			148.4		151.3				
α(C3–C4–C5)	120.6	119.7 ± 0.5	120.4 ± 1.0	108.1	122.2	128.0	120.2	132.8	125.5	109.4	112.8
α(O1–C5–C7)	114.0		112.9 ± 2.7	123.1	117.8	121.3	114.4	120.0	121.7	121.2	117.2
α(O1–C5–C4)	121.8	121.0 ± 0.8		120.6	120.7	116.9	121.3	117.0	122.1	120.4	120.5
α(O2–C3–C6)	119.7		118.7 ± 3.1	123.1	120.0	121.4	119.7	120.0	121.7	123.1	117.2
α(O2–C3–C4)	121.7	123.0 ± 0.7		120.6	121.5	122.0	121.4	117.0	122.1	120.6	120.5
δ(O1–C5–C3–O2)	0.0			138.4[e]	0.0	180.0	0.0	18.2	−30.1	144.5	0.0
δ(C7–C5–C4–C3)	180.0			−90.4	180.0	0.0	180.0	6.6	163.8	−92.2	180.0
δ(C6–C3–C4–C5)	180.0			−90.4	180.0	180.0	180.0	6.6	163.8	−82.0	180.0

Distances (d) in angstroms and angles (α, δ) in degrees. The theoretical structures were optimized at the B3LYP/cc-pVTZ level.

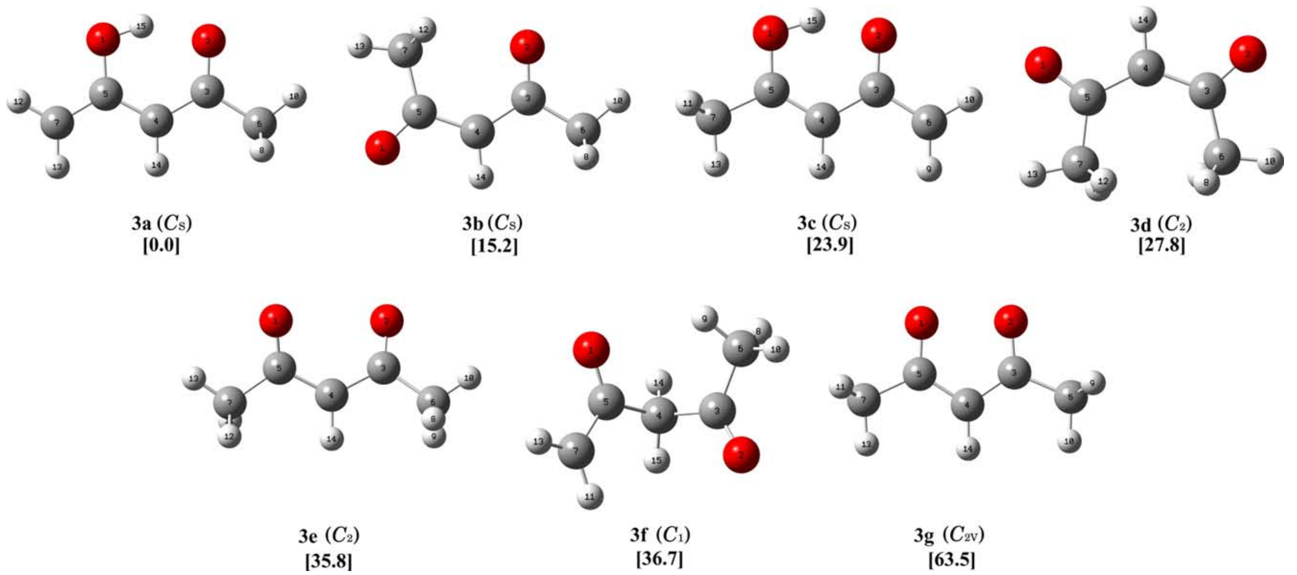
[a] From Ijima et al. [22].

[b] The final refined geometry for ground state of the enol tautomer (see Fig. 2 of Ref. [23]) suggests a C_1 structure, whereas our calculation leads to a C_s geometry. Differences can be related to the fact that data from Refs. [23,24] correspond to thermally averaged structures.

[c] From Camerman et al. [25].

[d] From Boese et al. [26].

[e] For the keto tautomer the d(O1–O2) distance is $\sim$3.502 Å and the δ(O1–C5–C3–O2) dihedral angle is 104.7° [23], whereas the present B3LYP/cc-pVTZ calculations predict that d(O1–O2) is 4.012 Å and δ(O1–C5–C3–O2) is 138.4°.



3a (C_s) [0.0]

3b (C_s) [15.2]

3c (C_s) [23.9]

3d (C_2) [27.8]

3e (C_2) [35.8]

3f (C_1) [36.7]

3g (C_{2v}) [63.5]

Fig. 2. Structures of seven conformers (**3a**–**g**) of the acac radical optimized at the B3LYP/cc-pVTZ level. The enthalpies relative to the most stable radical conformer (**3a**) (in brackets) were calculated at the CBS-QB3-tz level.

Table 2
Thermochemical properties of Hacac and acac radical in the gas phase, at 298 K

	B3P86[b]	CBS-QB3	CBS-QB3-tz
$\Delta_\mathrm{r}H^\circ$(enol → keto)	33.5	13.7	13.7
Bond homolysis			
DH°(acac–H)$_\mathrm{enol}$	382.4	378.3	380.2
$\Delta_\mathrm{f}H^\circ$(acac,g)	−220.0	**−224.1**	**−222.2**
DH°(acac–H)$_\mathrm{keto}$	348.8	364.7	366.5
$\Delta_\mathrm{f}H^\circ$(acac,g)	−243.6	**−227.7**	**−225.9**
Isogyric ($R = OH$)[c]			
$\Delta_\mathrm{r}H^\circ$	−120.5	−120.1	−118.5
DH°(acac–H)$_\mathrm{enol}$	376.7	377.0	378.7
$\Delta_\mathrm{f}H^\circ$(acac,g)	−225.7	**−225.4**	**−223.7**
Isogyric ($R = C_2H_5O$)[c]			
$\Delta_\mathrm{r}H^\circ$	−57.3	−67.0	−65.8
DH°(acac–H)$_\mathrm{enol}$	382.3	372.6	373.8
$\Delta_\mathrm{f}H^\circ$(acac,g)	−220.1	**−229.8**	**−228.6**
Isodesmic and isogyric ($R = CH_2CHO$)[c]			
$\Delta_\mathrm{r}H^\circ$	−48.6	−33.9	−32.5
DH°(acac–H)$_\mathrm{keto}$	344.7	359.4	360.8
$\Delta_\mathrm{f}H^\circ$(acac,g)	−247.7	**−233.0**	**−231.6**
Isodesmic and isogyric ($R = CH_2OH$)[c]			
$\Delta_\mathrm{r}H^\circ$	−52.3	−40.7	−38.9
DH°(acac–H)$_\mathrm{keto}$	350.2	361.8	363.6
$\Delta_\mathrm{f}H^\circ$(acac,g)	−242.2	**−230.6**	**−228.8**
Isodesmic and isogyric ($R = CH_2CH$)[c]			
$\Delta_\mathrm{r}H^\circ$	−115.0	−98.3	−96.5
DH°(acac–H)$_\mathrm{keto}$	348.2	364.9	366.7
$\Delta_\mathrm{f}H^\circ$(acac,g)	−244.2	**−227.5**	**−225.7**

Reaction enthalpies ($\Delta_\mathrm{r}H^\circ$), bond dissociation enthalpies (DH°), and enthalpies of formation ($\Delta_\mathrm{f}H^\circ$) in kJ/mol.[a]

[a] Selected values in bold.

[b] Extrapolated value based on the power law expression $E_X = E_\infty + A_3X^{-3} + A_5X^{-5}$ and B3P86/cc-pVXZ //B3LYP/cc-pVTZ (X = T,Q,5) single-point energy calculations. Thermal corrections from B3LYP/cc-pVTZ optimizations.

[c] $\Delta_\mathrm{r}H^\circ$ refers to reaction (7). Experimental data used to derive the bond dissociation enthalpies (in kJ/mol): DH°(HO–H) = 497.1 [29]; DH°(C_2H_5O–H) = 439.6 [29]; DH°(CH_2CHO–H) = 393.3 [8]; DH°(CH_2OH–H) = 402.5 [29]; DH°(CH_2CH–H) = 463.2 [8].

ference should be equal to zero. Based on bond homolysis reactions, for example, it is observed that the difference is ∼20 kJ/mol for the DFT method, whereas it amounts to less than 4 kJ/mol using the CBS methods.

Our selected value for $\Delta_f H^\circ$(acac,g) and the experimental enthalpies of formation of the gaseous Hacac tautomers imply that $DH^\circ(\text{acac–H})_{\text{enol}}$ is 375 ± 8 kJ/mol and $DH^\circ(\text{acac–H})_{\text{keto}}$ is 365 ± 8 kJ/mol. The former result is quite close to the acidity-based estimate by Sharpe and Richardson (368 ± 25 kJ/mol) [6], and the early prediction by Cavell and Pilcher (365 kJ/mol) [9], but it is significantly lower than the prediction by Irving and Ribeiro da Silva (418 ± 25 kJ/mol) [7]. However, more recent publications by Ribeiro da Silva's group [2] have adopted the value by Sharpe and Richardson. We should finally stress that our calculations show that the most stable radical (**3a**) is not generated by the O–H bond homolysis of the enol form (**1**), but rather by the C–H bond homolysis.

4. Conclusions

Theoretical results for the structure and thermochemical properties of Hacac (enol and keto forms) were compared with available experimental information. The results were based on DFT calculations extrapolated to complete basis-set and ab initio composite procedures CBS-QB3. A modified procedure that we named CBS-QB3-tz was also used. The enthalpy associated with the Hacac enol–keto tautomerisation predicted by CBS composite procedures is in good agreement with experiment, whereas extrapolated DFT calculations overestimate this quantity by ∼22 kJ/mol.

Special emphasis was placed on the calculation of the acac–H bond dissociation enthalpy and on the enthalpy of formation of the acac radical. We believe that our estimates based on the CBS composite procedures are presently the most accurate values.

The enthalpy of formation of gaseous acac, $\Delta_f H^\circ$(acac,g), was estimated as −228.3 kJ/mol (CBS-QB3) and −226.7 kJ /mol (CBS-QB3-tz). Based on these results, our recommended value is -227 ± 8 kJ/mol. The corresponding O–H and C–H bond dissociation enthalpies in acetylacetone are $DH^\circ(\text{acac–H})_{\text{enol}} = 375 \pm 8$ kJ/mol and $DH^\circ(\text{acac–H})_{\text{keto}} = 365 \pm 8$ kJ/mol, respectively. These results support an experimental gas-phase estimate by Sharpe and Richardson, $DH^\circ(\text{acac–H})_{\text{enol}} = 368 \pm 25$ kJ/mol, and imply that many literature values reported for metal–acac bond dissociation enthalpies in coordination complexes should be revised. Moreover, according to our calculations, the most stable radical structure is generated by the C–H bond homolytic dissociation of the enol form.

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