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Computational Study on the Bond Dissociation Enthalpies in the Enolic and Ketonic Forms of β-Diketones: Their Influence on Metal−Ligand Bond Enthalpies

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A computational study on the thermodynamic properties of 13 β-diketones is presented. The B3LYP//6-311+G(2d,2p)//B3LYP/6-31G(d) theoretical approach was employed to compute the O−H and C−H bond dissociation enthalpies and enthalpy of tautomerization and to estimate standard gas-phase enthalpies of formation for the radicals and for the parent molecules. The gas-phase enthalpies of formation for the neutral molecules are in excellent agreement with available experimental data, supporting the estimates made for the radicals. The latter are very important for the clarification of the thermochemistry of many β-diketonato metal complexes previously reported in the literature. Importantly, when substituents R = −CHR′ are attached to the β-diketone's scaffold, C−H homolytic bond cleavage is always favored with respect to O−H bond scission.

1. Introduction

The strengths of bonds between transition metals or metallic ions and ligands are of deep interest due to their involvement in important chemical and biological processes[1,2] and have been widely studied in the past years both by experimental and by computational techniques.[3−11]

Among the large number of ligands appears the family of β-diketones, which in general are bidentate ligands and which are known to form complexes with almost all metal atoms in the periodic table of elements.[12] The smaller β-diketone is the acetylacetone (pentane-2,4-dione) species with its thermochemistry (condensed-phase and gas-phase) reported in the literature.[13−16] This compound, as well as other β-diketones, can exist in a keto/enol tautomeric equilibrium as illustrated in the scheme below. The enol may exist in two different conformations depending on whether R_1 is equal, or not, to R_2; in acetylacetone, $R_1 = R_2 = CH_3$ and $R_3 = H$.

The enolic form (rather than the keto) is generally the most stable conformation due to its six-member cyclic structure fulfilled by an internal O−H···O hydrogen bond; in the case of acetylacetone, a very recent critical analysis of data available in the literature together with new correlation gas chromatography experiments performed by Temprado et al.[17] resulted in a gas-phase energetic difference between the enol and the keto tautomers of 19.3 ± 2.8 kJ/mol. This value is identical to that based on the intensity ratios from older gas-phase ^{1}H NMR experiments by Folkendt et al,[18] $\Delta H°$ (keto−enol) = 19.5 ± 0.8 kJ/mol, and to that determined also by Temprado et al. for the tautomers in the liquid state. A much lower value (10.0 ± 0.8 kJ/mol) was published earlier by Powling and Bernstein as retrieved from infrared analytical experiments carried out at $T = 386$ K.[19] Very recently, Cabral do Couto et al. computed the enthalpic difference between the acetylacetone's keto and enol forms at the B3P86/cc-pVXZ//B3LYP/cc-pVTZ level of theory and with the CBS-QB3 composite approach.[20] A difference of 33.5 kJ/mol was computed with the hybrid-density functional method while a smaller difference of 13.7 kJ/mol was computed with the, in principle much more accurate, composite approach.

In solution, the enol form of the different β-diketones loses its proton and the resulting anion is the species that complexes with metals according to the reaction below:

$$n\,\mathrm{H}\beta\text{-dik (l or cr)} + \mathrm{MX}_n \cdot x\mathrm{H_2O\ (cr)} + y\,\mathrm{H_2O\ (l)} \rightarrow \mathrm{M}(\beta\text{-dik})_n\ \mathrm{(cr)} + n\,\mathrm{HX} \cdot [(x+y)/n]\mathrm{H_2O\ (l)} \quad (1)$$

where n is the number of ligands chelated to the metal ion. The latter comes from a solution obtained by dissolution of a pure sample of another complex with the same metal, which may be, or not, hydrated with x water molecules.

Many works concerning the determination of the energetics of the metal−ligand bonds are easily found in the literature.[5] In the case of the complexes between metals and β-diketones, the metal−ligand bond strength is obtained from the equation below:

$$\mathrm{M}(\beta\text{-dik})_n\ \mathrm{(g)} \rightarrow \mathrm{M\ (g)} + n\,\beta\text{-dik}^{\bullet}\ \mathrm{(g)} \quad (2)$$

Please notice that the metal−oxygen bond strength is a mean value of the $2n$ bonds between the metal and the β-diketone; that is, it is the bond dissociation enthalpy of the gaseous homolytic dissociation, reaction 2, divided by $2n$. The bond dissociation enthalpy is obtained from the experimental gas-phase enthalpies of formation of the species included in reaction 2. The standard gas-phase enthalpy of formation (at $T = 298.15$ K) of the complex is obtained by solution and reaction calorimetry and by Knudsen effusion or Calvet microcalorimetry. The gas-phase enthalpies of formation of the metal atoms are already known from the literature. The standard gas-phase enthalpy of formation for the β-diketone radical (β-dik$^{\bullet}$) is estimated from the reaction below:

$$\mathrm{H}\beta\text{-dik (g)} \rightarrow \mathrm{H\ (g)} + \beta\text{-dik}^{\bullet}\ \mathrm{(g)} \quad (3)$$

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TABLE 1: Selected Bond Lengths and Bond Angles, Computed at the B3LYP/6-311+G(2d,2p) Level of Theory, for the Enolic Forms of All β-Diketones Considered in the Present Work[a]

	distances						angles				
compound[b]	O_1-H_1	O_1-C_1	C_1-C_2	C_2-C_3	C_3-O_2	O_2-H_1	$H_1-O_1-C_1$	$O_1-C_1-C_2$	$C_1-C_2-C_3$	$C_2-C_3-O_2$	$C_3-O_2-H_1$
Hacac	1.009	1.328	1.372	1.444	1.249	1.637	105.7	122.3	120.6	121.9	100.5
Hmeacac	1.014	1.328	1.382	1.452	1.253	1.573	105.8	122.5	118.2	122.5	100.9
Htfac ($R_2 = -CF_3$)	0.998	1.319	1.375	1.422	1.237	1.656	107.1	121.8	119.6	124.9	98.6
Hhfac	0.993	1.315	1.358	1.439	1.227	1.707	107.0	125.1	118.5	124.4	100.1
Hdibm	1.013	1.327	1.376	1.441	1.254	1.612	105.7	121.8	120.6	121.6	100.6
Hpiprm ($R_2 = -Et$)	1.009	1.332	1.373	1.446	1.250	1.624	106.1	121.2	120.9	122.1	100.0
Hibpm ($R2 = -iPr$)	1.008	1.324	1.372	1.438	1.250	1.583	106.1	120.5	120.8	121.7	100.3
Hdpm	1.011	1.330	1.374	1.447	1.252	1.606	105.8	121.3	121.0	121.1	100.9
Hbzac ($R_2 = -Ph$)	1.006	1.323	1.369	1.440	1.252	1.602	105.6	122.2	120.7	120.6	101.6
Hdbzm	1.011	1.324	1.376	1.437	1.253	1.560	105.4	120.8	120.6	120.9	101.0
Hbztfac ($R_2 = -CF_3$)	1.005	1.317	1.355	1.453	1.347	1.611	104.8	125.1	119.3	119.7	103.2
Htfdmh ($R_2 = -CF_3$)	0.999	1.320	1.377	1.421	1.238	1.631	107.4	120.6	119.6	125.2	98.1
Httfa ($R_2 = -CF_3$)	1.010	1.327	1.389	1.420	1.249	1.629	106.7	121.4	119.1	125.1	98.5

[a] Units are Ångstroms and degrees. [b] The R_2 substituent is given in parentheses when $R_1 \neq R_2$, cf. Scheme 1. In all compounds, $R_3 = H$ except for Hmeacac where $R_3 = CH_3$. Hacac and Hmeacac, $R_1 = R_2 = CH_3$; Htfac, $R_1 = CH_3$; Hhfac, $R_1 = CF_3$; Hdibm, $R_1 = R_2 = CH(CH_3)_2$; Hpiprm, $R_1 = C(CH_3)_3$ and $R_2 = CH_2CH_3$; Hibpm, $R_1 = C(CH_3)_3$ and $R_2 = CH(CH_3)_2$; Hdpm, $R_1 = R_2 = C(CH_3)_3$; Hbzac, $R_1 = CH_3$ and $R_2 = C_6H_5$; Hdbzm, $R_1 = R_2 = C_6H_5$; Hbztfac, $R_1 = CF_3$ and $R_2 = C_6H_5$; Htfdmh, $R_1 = CF_3$ and $R_2 = C(CH_3)_3$; and Httfa, $R_1 = C_4H_3S$ and $R_2 = CF_3$.

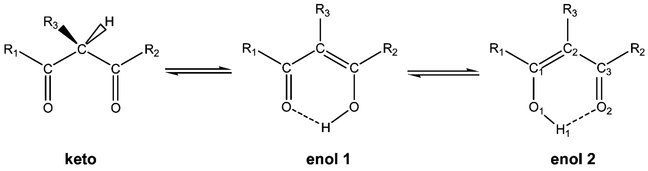
by using the experimental gas-phase enthalpies of formation of the β-diketone (H-dik) and of atomic hydrogen and a more or less accepted value for the gas-phase O−H or C−H bond dissociation enthalpies. As reported by Ribeiro da Silva,[5] several gas-phase O−H bond dissociation enthalpies appear in the literature, all different, and spanning a range of values between 365 and 460 kJ/mol. In that paper of Ribeiro da Silva,[5] a value of 418 ± 20 kJ/mol was considered for all β-diketones, even knowing that rather different R_1, R_2, and R_3 were present, namely, methyl, *t*-butyl, or phenyl groups among others. Therefore, the gas-phase O−H and C−H bond dissociation enthalpies have been computed, at the B3LYP/6-311+G(2d,2p)/B3LYP/6-31G(d) level of theory, for the following compounds: acetylacetone (Hacac), methylacetylacetone (Hmeacac), trifluoroacetylacetone (Htfac), hexafluoroacetylacetone (Hhfac), diisobutyrylmethane (Hdibm), pivaloylpropionylmethane (Hpiprm), isobutyrylpivaloylmethane (Hibpm), dipivaloylmethane (Hdpm), benzoylacetone (Hbzac), dibenzoylmethane (Hdbzm), benzoyltrifluoroacetone (Hbztfac), trifluoropivaloylmethane (Htfdmh), and tenoyltrifluoroacetone (Httfa), which have been considered in a previous publication.[5]

2. Computational Procedure

Density functional calculations at the B3LYP level of theory[21] have been performed for all compounds considered in the present work. A similar strategy to that previously employed in the computational thermochemistry of neutral and radical species of compounds containing N−H or O−H bonds has been used.[22,23] This is the combination of a 6-31G(d) basis set, to extract thermal corrections from a frequency calculation, and the 6-311+G(2d,2p) for further optimization of the geometry and to obtain the energy of each species. All calculations have been performed with the Gaussian 98 computer code.[24]

In the case of the open-shell radical species, the values of $<S^2>$ were carefully checked and found to be very close to 0.75, an indication of pure doublets states with no spin contamination. In all calculations, the absence of imaginary frequencies at the lower level of theory, B3LYP/6-31G(d), ensured that all structures were true minima on the potential energy surface; the optimization of geometries at the higher level of theory was started from these preoptimized structures. The enthalpy of each compound at $T = 298.15$ K used to extract the thermodynamic data in the forthcoming sections was the sum of the energy computed at the B3LYP/6-311+G(2d,2p) level of theory and the thermal corrections (zero-point energies, pV term, and translational, rotational, and vibrational contributions at $T = 298.15$ K) computed at the B3LYP/6-31G(d) level.

SCHEME 1: $R_1 = R_2 = R_3 = CH_3$ (Hmeacac)[a]



[a] R_3 is always H. $R_1 = R_2 = CH_3$ (Hacac); $R_1 = CH_3$ and $R_2 = CF_3$ (Htfac); $R_1 = R_2 = CF_3$ (Hhfac); $R_1 = R_2 = CH(CH_3)_2$ (Hdibm); $R_1 = C(CH_3)_3$ and $R_2 = CH_2CH_3$ (Hpiprm); $R_1 = C(CH_3)_3$ and $R_2 = CH(CH_3)_2$ (Hibpm); $R_1 = R_2 = C(CH_3)_3$ (Hdpm); $R_1 = Ph$ and $R_2 = CH_3$ (Hbzac); $R_1 = R_2 = Ph$ (Hdbzm); $R_1 = Ph$ and $R_2 = CF_3$ (Hbztfac); $R_1 = C(CH_3)_3$ and $R_2 = CF_3$ (Htfdmh); and $R_1 = C_4H_3S$ and $R_2 = CF_3$ (Httfa).

3. Results

3.1. Structural Data. Selected bond lengths and angles for the different β-diketones are reported in Table 1. Even if no symmetry constraints are introduced in the calculations (nosymm keyword in Gaussian code), the optimized geometry for the smallest β-diketone, Hacac, deeply studied in the past by theoretical and experimental methods,[20] is practically a C_s structure, as confirmed by the most recent experimental[25] and computational[20] studies. In fact, the largest deviation from planarity, measured by the different dihedral angles, is of only 0.1°. Furthermore, in disagreement with older studies, the distances between H_1 and O_1 (see Scheme 1 for atom numbering) or between H_1 and O_2 are different, ruling out the C_{2v} symmetric structure. The structure of the hexafluoroacetylacetone species, Hhfac, was also investigated previously, by gas-phase electron diffraction,[26] and by Moller−Plesset (MP*n*, $n = 2-4$) and configuration interaction (QCISD) methods.[27] The B3LYP/6-311+G(2d,2p) geometry is very nearly the same as the MP2 geometry reported by Sliznev et al.,[27] except the O_1-H_1 bond length, which is equal to 0.993 Å by density functional theory (DFT) computations and equal to 1.075 Å when the MP2 method is employed. Madsen and co-workers studied, by both experimental and computational methods, the most stable conformation of benzoylacetone.[28,29] Their X-ray and neutron diffraction data show that the enol's hydrogen atom of Hbzac sits asymmetrically between the two oxygen atoms with O···H

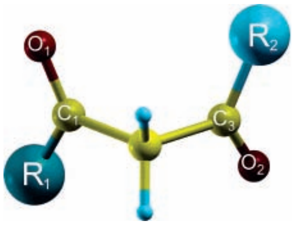


Figure 1. General scheme for the keto form of all β-diketones.

distances of 1.329 and 1.245 Å.[28] The most stable structure coming from their DFT calculations is, as expected, very similar to that reported in the present work, with two distinct RC−O−H and RC═O frames. Furthermore, they found a transition state with a structure that is similar to that coming from X-ray and neutron diffraction experiments, suggesting that the experimental geometry is a sum of two contributions, one with the hydrogen atom bonded to the oxygen atom closer to the methyl group (the most stable) and another with the hydrogen atom bonded to the oxygen atom nearer to the benzyl substituent. Another gas-phase electron diffraction study was found in the literature concerning the structure of Hacac and Htfac compounds[30] but contradicting the most recent findings; the model in best agreement with the diffraction data places the enol proton located symmetrically between the oxygen atoms.

The analysis of the full-set of structural parameters appearing in Table 1 permits one to observe tiny but important differences in the $R_1C(-OH)═C(-R_3)-C(═O)R_2$ moiety due to the presence of different R substituents. For example, the compounds with $R = -CF_3$ are the ones with smaller O_1-H_1 bond lengths, with the smaller observed when there are two of these substituents, cf., Hhfac, and this substitution is also connected with smaller O_1-C_1 distances. Furthermore, all compounds with $R_1 \neq R_2$ and with one $R = -CF_3$ are more stable if this substituent is attached to the carbon atom nearby the C═O bond.

In the case of the less stable keto forms, with structural parameters not given here but in the Supporting Information, a conformation similar to that depicted in Figure 1 is obtained for all compounds. Please note that when $R_1 = R_2$, except for the Hmeacac molecule where $R_3 \neq H$, the compounds have a C_2 symmetry.

The most important difference between the structures is the $O_1C_1C_3O_2$ dihedral angle. Their values are the following: Hacac, 140.9°; Hmeacac, 73.3°; Htfac, 96.6°; Hhfac, 66.0°; Hdibm, 136.9°; Hpiprm, 135.1°; Hibpm, 103.5°; Hdpm, 100.0°; Hbzac, 91.5°; Hdbzm, 166.0°; Hbztfac, 68.5°; Htfdmh, 71.9°; and Httfa, 66.8°.

The most stable geometries of the β-dik$^\bullet$ radical of Hacac are an enol form, Figure 2a, and a keto form, Figure 2b, where C−H and O−H bond cleavage, respectively, took place. The enol form depicted in Figure 2 for the β-dik$^\bullet$ radical of Hacac is also the most stable conformation for all other compounds, except for Hmeacac, i.e., the unique compound studied with $R_3═CH_3$. For the latter compound, a radicalar species with the unpaired electron located at the R_3's carbon atom, Scheme 1, is more stable than the conformation resembling Figure 2a by 3.8 kJ/mol and then the conformation resembling Figure 2b by 6.0 kJ/mol. The most stable conformation for the meacac$^\bullet$ radical (following the β-dik$^\bullet$ notation introduced in eqs 1−3) is the planar structure illustrated in Figure 3.

3.2. Bond Dissociation Enthalpies. The O−H and C−H enthalpies of dissociation, as well as the enthalpies of keto−enol tautomerism, are reported in Table 2. All values included in this table were calculated with the B3LYP/6-311+G(2d,2p)//B3LYP/6-31G(d) enthalpies, $T = 298.15$ K, compiled in the Supporting Information. Furthermore, dissociation enthalpies are calculated as the difference between the enthalpies of the products and reactants in eq 3 and, in accordance with previous works,[22,23,31−34] the enthalpy of the hydrogen atom is that based on the exact energy (−0.500000 au) with added thermal corrections for the reference temperature (5/2 *RT*).

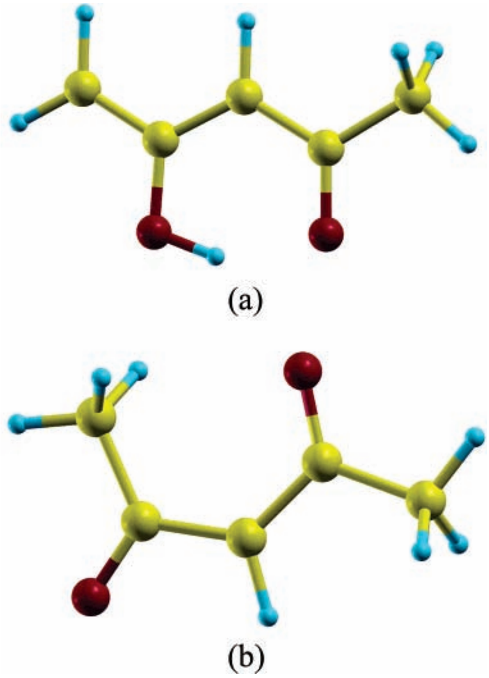


Figure 2. Two most stable enol (a) and keto (b) conformations for the radical of Hacac.

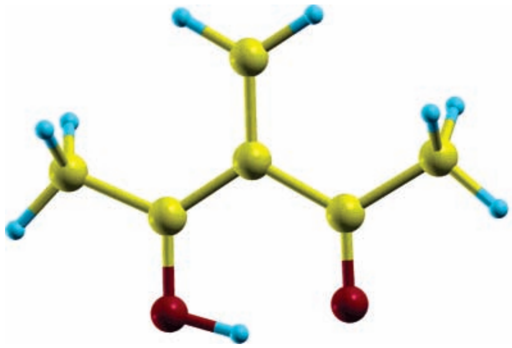


Figure 3. Most stable enol form for the radical of Hmeacac.

As written above, the enthalpies of dissociation of O−H and C−H bonds and the enthalpy to convert the enol form of Hacac to the keto form have been published very recently. Therefore, the discussion of the results reported in Table 2 will start with the comparison of present results and those reported by Cabral do Couto et al.[20] As noticed by these authors and also by Irikura et al.,[35] albeit the latter work is devoted to the acac anion, the most stable structure for the one hydrogen less Hacac species (acac radical or acac anion) is in the conformation illustrated by Figure 2a, i.e., with the hydrogen atom removed from the terminal methyl group (R_1). The C−H bond cleavage in the terminal methyl group has an enthalpy of 374.7 kJ/mol, cf. Table 2, in rather good agreement with the interval of results, 378.3−382.4 kJ/mol, reported by Cabral do Couto et al.[20] One should highlight here that in that work the authors employed more complete approaches demanding higher computational resources. In the present work, the choice of a less demanding approach is connected with the larger structure of the other compounds also studied here. Nevertheless, the small difference between

TABLE 2: Bond Dissociation and Tautomerization Enthalpies (kJ/mol) Computed at the B3LYP/6-311+G(2d,2p) Level of Theory, for the Enolic Forms of All β-Diketones Considered in the Present Work

	bond dissociation enthalpy[b]			
compound[a]	O−H	C−H[c]	C−H[d]	enthalpy of tautomerization
Hacac	397.8	374.7	482.0	23.9
Hmeacac	372.0	369.8	366.0	21.7
Htfac ($R_2 = -CF_3$)	402.7	375.3	488.9	34.6
Hhfac	413.1		493.5	32.2
Hdibm	395.2	343.0	481.2	26.7
Hpiprm ($R_2 = -Et$)	396.7	353.6	477.1	23.8
Hibpm ($R_2 = -iPr$)	399.9	344.9	477.4	32.4
Hdpm	409.9		471.9	30.0
Hbzac ($R_2 = -Ph$)	398.4	374.2	475.0	28.0
Hdbzm	407.8		470.0	22.8
Hbztfac ($R_2 = -CF_3$)	418.1		484.1	38.1
Htfdmh ($R_2 = -CF_3$)	414.0		484.0	45.9
Httfa ($R_2 = -CF_3$)	414.2		487.4	34.2

[a] For more structural details, see the footnote of Table 1. [b] All values calculated with respect to the most stable enol form. [c] C−H scission at the R_1 or R_2 substituents, depending on the orientation and stability of the O−H bond in the radical. [d] C−H scission at the R_3 substituent.

the B3LYP/6-311+G(2d,2p)//B3LYP/6-31G(d) bond dissociation enthalpy and that resulting from CBS-QB3 computations, 378.3 kJ/mol, or from CBS-QB3-tz computations, 380.2 kJ/mol,[20] seems to guarantee enhanced confidence on the DFT results herewith presented.

Because the keto form is less stable than the enol form, the β-dik−H bond dissociation enthalpy will be much smaller if the keto form is used as the reference state; to use the keto form as the reference state, one only needs to subtract the keto−enol enthalpy of tautomerization to the β-dik−H bond dissociation enthalpy given in Table 2. The enthalpy of tautomerization for Hacac, computed at the B3LYP level of theory, is 23.9 kJ/mol, a value that is close to the, in principle, more accurate experimental result due to Temprado et al., $\Delta H°$ (keto−enol) = (19.3 ± 2.8 kJ/mol) kJ/mol.[17] Our computed value lands between the two computed numbers published by Cabral do Couto et al., 13.7 and 33.5 kJ/mol, with CBS-QB3(-tz) and B3P86/ccpVXZ//B3LYP/cc-pVTZ (X = T, Q, 5) approaches, respectively.

The O−H enthalpy of dissociation is ∼23 kJ/mol larger than that required to extract the hydrogen atom from the R_1 group. The B3LYP computed value is 397.8 kJ/mol, which is not far from the CBS-QB3(-tz) results (392−394 kJ/mol) published earlier in the literature.[20] The very good comparison of present B3LYP results with previously published experimental data and with the CBS-QB3 results suggests that the DFT approach used in this work is enough for the aim of this work, which is the computation of the gas-phase β-dik−H bond dissociation enthalpy. The C−H bond dissociation enthalpy was also computed for the reaction producing the β-dik$^\bullet$ radical with R_3 = H removed. The C−H bond dissociation enthalpy is now 482.0 kJ/mol, showing that this kind of radical is highly unstable. However, if the R_3 group in Hacac is changed to CH_3, the Hmeacac entry in Table 2, the radical formed is much more stable if the hydrogen atom is removed from R_3 (Figure 3) than from R_1 or from O−H. However, the difference between the enthalpies of these three radicals is only 6 kJ/mol. This small difference between the enthalpies of the three possible radicals contrasts with that written above for the similar Hacac compound. In the case of the Hmeacac species, the keto−enol enthalpy of tautomerization is 21.7 kJ/mol.

For all other compounds in Table 2, with hydrogen atoms directly attached to the carbon atom bonded to the $-C({=}O)C(-H){=}C(-OH)-$ moiety, the radicals coming from C−H bond cleavage at that position are always more stable than radicals formed by O−H bond scission or from removal of the hydrogen atom attached to C_2. When H is removed from C_2, β-dik−H bond dissociation enthalpies are larger than 470 kJ/mol. This is due to the fact that when R_3 = H, the removal of the hydrogen atom at C_2 produces a vinylic radical, which is very unstable, whereas when $R_3 = CH_3$, the allylic radical formed after C−H bond cleavage is very stable; therefore, a small enthalpy of dissociation is calculated.

The full analysis of all compounds with R_3 = H shows the following: (i) the presence of one or two CF_3 groups leads to the increase of the O−H bond dissociation enthalpy; (ii) smaller increments are also found when methyl groups are replaced by phenyl groups; (iii) substitution of a *tert*-butyl group by a 2-thenoyl substituent has similar effects on both O−H and C−H bond dissociation enthalpies; and (iv) substitution by isopropyl substituents turns easier β-dik−H bond cleavage by C−H scission at the isopropyl group, i.e., $R_4CH(CH_3)_2 \rightarrow R_4C(CH_3)_2 + H$. One final but important conclusion from the complete analysis of Table 2 is that the keto−enol enthalpy of tautomerization changes appreciably by varying R_1 and R_2 groups. When R_3 = H, the lowest $\Delta H°$ (keto−enol) result is found for Hdbzm ($R_1 = R_2$ = Ph), 22.8 kJ/mol, and the highest difference is found for the Htfdmh compound (R_1 = *tert*-butyl and $R_2 = CF_3$); the latter value is 45.9 kJ/mol. Even that the use of different computational methods point to different keto−enol enthalpies of formation, the latter observation shows that the use of the same $\Delta H°$ (keto−enol) for different $R_1C({=}O)C(-H){=}C(-OH)$-R_2 compounds, in order to retrieve additional thermodynamic information, is not advisable. Previously, Ribeiro da Silva et al. assumed that the gas-phase enthalpy of enolization of pentan-2,4-dione [$\Delta H°$ (keto−enol) = 10.0 kJ/mol] could be applied to a series of different β-diketones, some of which are also object of the present study.[36] With this assumption, they tried to see if a group energy scheme could be used to estimate the gas-phase enthalpies of formation of the β-diketones with group bond-energy terms based on an earlier work of Cox and Pilcher.[37] In that work of Ribeiro da Silva et al.,[36] the comparison between the experimental enthalpies of formation of the enols to which the $\Delta H°$ (keto−enol) = 10.0 kJ/mol was added and the estimated results from the Cox and Pilcher scheme showed larger differences for compounds such as that with $R_1 = R_2 = CF_3$ and smaller deviations for compounds such as that with $R_1 = R_2$ = *tert*-butyl or with R_1 = *tert*-butyl and R_2 = ethyl. Although this seems to be not conclusive, the differences reported by Ribeiro da Silva and co-workers appear to be affected by the use of the same $\Delta H°$ (keto−enol).

3.3. Gas-Phase Enthalpies. The standard gas-phase enthalpies of formation for the different Hβ-dik compounds with R_3 = H have been estimated from the computed enthalpy of the gas-phase substitution reaction below:

$$R_1C({=}O)C(-H){=}C(-OH)R_2 + n\,CH_3C({=}O)CH_3 \rightarrow CH_3C({=}O)C(-H){=}C(-OH)CH_3 + R_1C({=}O)CH_3 + R_2C({=}O)CH_3 \quad (4)$$

and the experimental enthalpies of formation of $CH_3C({=}O)C(-H){=}C(-OH)CH_3$ (Hacac), $\Delta_f H_m° = -378.2 \pm 1.2$ kJ mol^{-1};[17] $CH_3C({=})CH_3$, $\Delta_f H_m° = -217.1 \pm 0.5$ kJ mol^{-1};[38] $CH_3CH_2C({=}O)CH_3$, $\Delta_f H_m° = -238.5 \pm 0.9$ kJ mol^{-1};[39] $(CH_3)_2CHC({=}O)CH_3$, $\Delta_f H_m° = -262.57 \pm 0.87$ kJ mol^{-1};[39] $(CH_3)_3$-

TABLE 3: Gas-Phase Enthalpies of Formation (kJ/mol) for the Different Hβ-dik Compounds with $R_3 = H$ and Their Corresponding Radicals, Estimated at the B3LYP/6-311+G(2d,2p)//B3LYP/6-31G(d) Level of Theory

	Hβ-dik			β-dik$^{\bullet}$
compound[a]	computational	experimental	Δ[b]	computational
Htfac ($R_2 = -CF_3$)	−995.7	−997.3 ± 2.3[c]	−1.6	−840.0
		−1003.3 ± 3.3[d]	−7.6	−846.0
Hhfac	−1597.4	−1592.4 ± 4.3[c]	5.0	−1397.3
Hdibm	−471.4	−470.4 ± 2.1[e]	1.0	−354.4
Hpiprm ($R_2 = -Et$)	−472.8	−470.9 ± 2.3[e]	1.9	−335.3
Hibpm ($R_2 = -{}^{i}Pr$)	−499.2	−510.7 ± 2.1[e]	−11.5	−383.8
Hdpm	−525.7	−528.4 ± 3.9[e]	−2.7	−336.5
Hbzac ($R_2 = -Ph$)	−246.9	−244.1 ± 2.9[f]	2.8	−87.9
		−251.3 ± 2.9[e]	−4.4	−95.1
Hdbzm	−113.3	−109.2 ± 2.0[f]	4.1	80.6
Hbztfac ($R_2 = -CF_3$)	−867.5	−865.6 ± 4.2[f]	1.9	−665.5
computational		−875.2[d]	−7.7	−675.1
Htfdmh ($R_2 = -CF_3$)	−1071.1	−1074.1 ± 5.6[c]	−3.0	−878.1
Httfa ($R_2 = -CF_3$)	−840.9	−862.4 ± 4.2[g]	−21.5	−666.2

[a] For more structural details, see the footnote of Table 1. [b] Difference between experimental and computational values. [c] Ref 36. [d] Ref 50. [e] Ref 40. [f] Ref 41. [g] Ref 51.

$CC(=O)CH_3$, $\Delta_f H_m° = -290.67 \pm 0.88$ kJ mol^{-1};[39] and $C_6H_5C(=O)CH_3$, $\Delta_f H_m° = -86.7 \pm 1.7$ kJ mol^{-1}.[39]

In eq 4, $n = 1$ or 2 and depends on the number of methyl groups replaced in Hacac to obtain the other $R_1C(=O)C(-H)=C(-OH)R_2$ compounds. Furthermore, experimental standard gas-phase enthalpies of formation for $CF_3C(=O)CH_3$ and $C_4H_3SC(=O)CH_3$ were not found in the literature. To obviate this problem, the G3MP2B3 method was used to compute their $\Delta_f H_m°$ based on the atomization reaction and the experimental enthalpies for the atoms taken from ref 39. The use of the atomization reaction here is due to the fact that we could not find in the literature any enthalpy of formation for a compound with a CF_3 group near a C=O bond, unless some β-diketones, which would allow the use of isodesmic reactions. Results were obtained as follows: $\Delta_f H_m°[CF_3C(=O)CH_3] = -834.7$ kJ/mol; $\Delta_f H_m°[C_4H_3SC(=O)CH_3] = -65.4$ kJ/mol. The G3MP2B3 method seems to be adequate for these estimations since the G3MP2B3-computed enthalpy of formation for acetone is −214.6 kJ/mol, in excellent agreement with the four experimental results retrieved from ref 39; the difference between the G3MP2B3 result and the selected value given in the review of Pedley[38] is of only 2.8 kJ/mol.

The gas-phase enthalpies estimated with one of the approaches given above for all of the Hβ-dik compounds (except Hacac) are reported in Table 3. The agreement between theoretical numbers and all experimental data is rather satisfactory, with a mean Δ smaller than 5.5 kJ/mol, and the agreement is even better if larger Δ are disregarded when there is more than one experimental result. In fact, only for two compounds, Hibpm and Httfa, the difference between computed and at least one experimental value is always lower than the mean value given above. This excellent comparison between theoretical and experimental gives further support to the computational approach used. When more than one experimental result is available for a specific compound, entries Htfac, Hbzac, and Hbztfac, the picture coming from the analysis of Table 3 suggests that the tautomeric equilibrium possible in this kind of compound introduces strong difficulties for the experimental determination of thermodynamic parameters. For instance, Ribeiro da Silva et al.[40,41] have used two different experimental techniques for the determination of the standard molar enthalpies of sublimation for Hbzac and, as it is shown in Table 3, two enthalpies of formation, differing by ~7 kJ/mol, have been obtained with the computational result positioned between these two results. The general good agreement between computed and experimental results suggests that the enthalpy of formation estimated for Hibpm could be more accurate than the experimental result. However, in the case of the Httfa compound, for which it is found the largest difference between estimated and experimental values, the analysis is somewhat different since one must consider that the estimated enthalpy of formation for the $C_4H_3SC(=O)CH_3$ anchor species used together with reaction 4 could be affected by significant errors due to the use of the G3MP2B3 and atomization reaction approach for its estimation. In fact, the mean deviation between G3MP2 and experimental results for five molecules containing sulfur, but smaller than $C_4H_3SC(=O)CH_3$, is of 8.1 kJ/mol;[42] for example, in the case of 2-methyl thiophene, the G3MP2 and experimental values differ by 9.2 kJ/mol. Despite the impossibility of a direct comparison of the estimated enthalpy for $C_4H_3SC(=O)CH_3$ with any experimental value, one is forced to look at a very recent study[43] where the performance of the G3MP2B3 computational approach was checked by its ability for the estimation of the enthalpy of formation of several small organosulfur compounds. In that study, the largest difference was of ~6 kJ/mol (computed value less positive than experimental result); therefore, the experimental result for Httfa is suggested to be included in future compilations of thermodynamic results.

The most important conclusion from Table 3 is that the theoretical approach seems to be reliable for the determination of standard enthalpies of formation for this kind of compound. Therefore, the same approach is used to estimate the enthalpies of formation of the radicals by the consideration of reaction 3. The enthalpy of reaction 3 is the same as the O−H or C−H bond dissociation enthalpies given in Table 2. The lowest bond dissociation enthalpy value for each entry in Table 2 must be used since in the thermochemistry of the gas-phase reaction described by eq 3 only the most stable conformations for the Hβ-dik, H, and β-dik$^{\bullet}$ species are important. Thus, using the bond dissociation enthalpies from Table 2, the experimental gas-phase enthalpy of formation for atomic hydrogen, $\Delta_f H_m° = 218.00$ kJ/mol,[44] and for Hβ-dik given in Table 3, the enthalpies of formation of the β-dik$^{\bullet}$ radicals were obtained. The gas-phase enthalpies of formation of Hacac and Hmeacac are not given in Table 3; the former is $\Delta_f H_m° = -378.2 \pm 1.2$ kJ mol^{-1},[39] and the latter is $\Delta_f H_m° = -428.9$ kJ mol^{-1}.[39] Starting with the smaller Hβ-dik compound studied here, Hacac, the enthalpy of formation of the acac radical is −221.5 kJ/mol. If the older experimental enthalpy of formation for Hacac determined by Hacking and Pilcher[16] is used, the enthalpy of formation of the acac radical is −227.7 kJ/mol. This latter result matches the result proposed by Cabral do Couto et al., $\Delta_f H_m°(\text{acac,g}) = -227 \pm 8$ kJ/mol, which is based on the result of Hacking and Pilcher for the Hacac compound and on the consideration of six different well-chosen reactions, bond homolysis, isogyric, isodesmic, and isogyric.[20] The results for the other β-dik$^{\bullet}$ compounds are reported in the rightmost column in Table 3 except that with $R_3 = CH_3$. For the meacac$^{\bullet}$ radical, the estimated gas-phase enthalpy of formation is −280.9 kJ/mol. If the enthalpic difference found for Httfa is neglected and considering the general excellent agreement between theoretical and what seem to be the best experimental enthalpies of

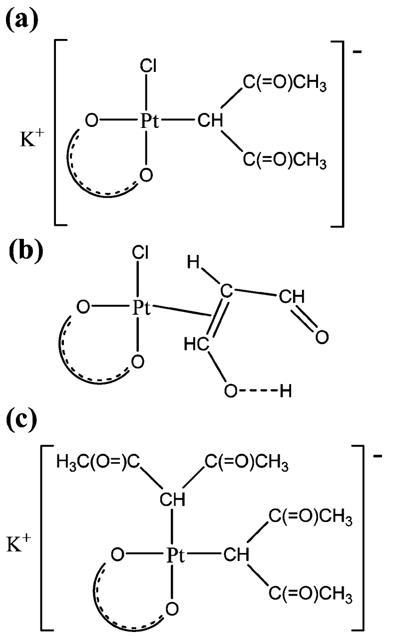


Figure 4. Carbon-bonded β-diketonato complexes with platinum.

formation for the Hβ-dik compounds, the estimated enthalpies of formation reported in Table 3 for the radicals are proposed to have an uncertainty of ±5 kJ/mol and may be used to obtain the M-β-dik bond dissociation enthalpies for the metal complexes reported in ref 5.

3.4. Formation of β-Diketonato Complexes. The complexes between transition metal and β-diketones usually involve a chelate where the metal atom is bonded to the β-diketone's oxygen atoms. A few important examples are reported in the literature where complexes involve at least one ligand bonded through a carbon atom.[12,45] The first β-diketonato complex containing a metal−carbon bond was prepared by Werner more than 100 years ago.[12] It was of the type K[PtCl(acac)$_2$] with its structure revealed more recently,[46] cf. Figure 4a. The latter complex in acid may adopt the impressive structure illustrated in Figure 4b, i.e., with one Pt−// bond.[12] Another interesting complex is that formed by the bonding of three acac ligands with the structure shown in Figure 4c.[47] A few other β-diketonato complexes with other metals (Se, Te, Mn, Au) and with at least one metal−carbon bond were also reported,[12] but their number is low when compared with the O-bonded complexes. Therefore, the β-dik$^\bullet$ radicals, which chelate metal atoms, adopt a keto form at least in solution. Thus, it seems interesting to calculate the energetic barrier for the reaction producing the keto form of β-dik$^\bullet$ (Figure 2b) from the corresponding enol (Figure 2a). The energetic profile that is depicted in Figure 5 was computed at the B3LYP/6-31G(d) level of theory with an additional single-point calculation at the B3LYP/6-311+G(2d,2p) within a cavity of water modeled by a self-consistent reaction field (SCRF) model.

In the SCRF environment simulating water, the energetic difference between the enol and keto forms of the acac$^\bullet$ radical is of 14.3 kJ/mol, showing that the reaction is thermodynamically possible. However, the kinetics for the intramolecular proton-transfer reaction introduces one important difficulty for the occurrence of this reaction since one of the barriers amounts to 226.9 kJ/mol, suggesting that a mechanism involving water molecules will be preferred. Very recently, Chen et al.[48] studied by theoretical methods the isomerization, dissociation, and dehydration reactions for Hacac and found a similar energetic profile for the enol→keto reaction, with a large barrier between the intermediate species and the keto conformation of acetylacetone. The explanation for such a large barrier found in these two situations is probably due to specific solvation effects,[49] not considered in the simple solvation model used here, which may have an important effect on the decrease of the intramolecular hydrogen O−H⋯O bond strength, thus lowering the reaction barrier. In fact, the consideration of a single water molecule has important influence on the calculated barriers. As included in Figure 6, the inclusion of a water molecule that acts as a spectator almost does not change the energetic barrier (decrease of only 5 kJ/mol) but an important effect is found when the water molecule is allowed to react with the acac radical. In the latter situation, the B3LYP/6-31G* energy barrier for hydrogen transfer from the O atom to the neighbor C-end atom in acac radical decreases by 60 kJ/mol and turns to be 116 kJ/mol. Therefore, an even smaller barrier is expected for the system where much more water molecules interact directly with the radical.

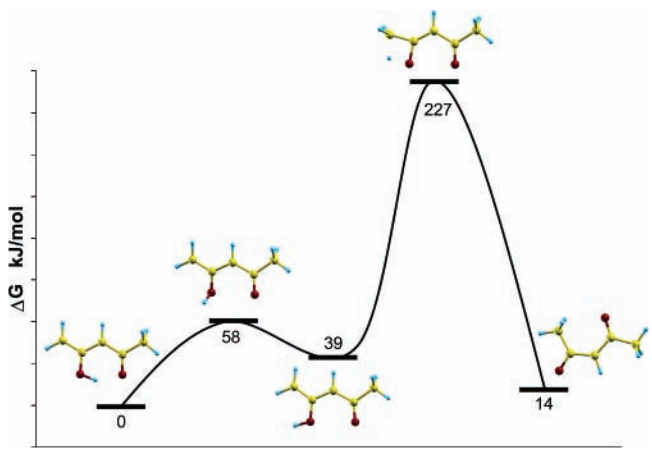


Figure 5. Energetic profile for the H transfer from the enolic acac radical to the ketonic acac radical. The SCRF model has been used to simulate the solvation effects of water.

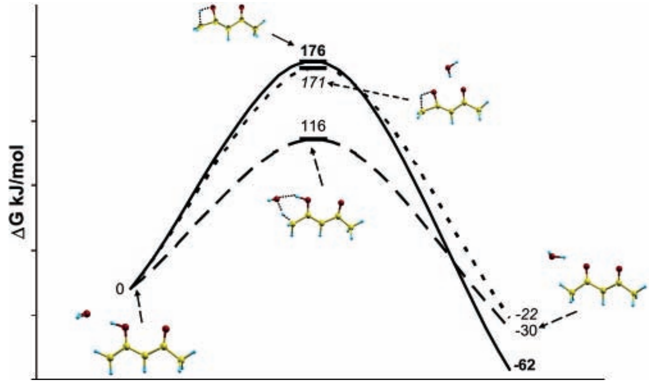


Figure 6. Energetic barrier for H transfer from the enolic oxygen atom of the acac radical to the nearest and terminal carbon atom computed at the B3LYP/6-31G(d) level of theory. Full line and text in bold, absence of water molecule; dotted line and text in italic, in the presence of a water molecule acting as a spectator; and dashed line and normal text, in the presence of a water molecule with an active role in the reaction.

The β-diketonato complexes involve the coordination with the β-dik$^\bullet$'s oxygen atoms in a cis conformation, which is not the most stable structure for these radicals, formed by O−H homolytic dissociation, which adopt a preferential *trans* conformation similar to that reported in Figure 2b for acac. The enthalpy required to obtain a planar *cis*-β-dik$^\bullet$ (O−H bond scission) radical from its most stable trans conformation is given in Table 4. The values are of about 20−30 kJ/mol and

TABLE 4: Enthalpy (kJ/mol) Required to Obtain a Planar *cis-β*-dik$^\cdot$ Radical from a *trans-β*-dik$^\bullet$ Radical

compound[a]	enthalpy	angle[b]	compound[a]	enthalpy	angle[b]
Hacac	25.4	179.9	Hdpm	10.0	129.0
Hmeacac	47.0	180.0	Hbzac (R_2 = −Ph)	28.9	173.0
Htfac (R_2 = $-CF_3$)	30.6	179.6	Hdbzm	23.0	114.8
Hhfac	24.2	179.7	Hbztfac (R_2 = $-CF_3$)	20.2	132.1
Hdibm	26.7	165.4	Htfdmh (R_2 = $-CF_3$)	23.3	124.7
Hpiprm (R_2 = −Et)	29.3	179.5	Httfa (R_2 = $-CF_3$)	21.6	147.8
Hibpm (R_2 = $-{}^{i}Pr$)	23.2	171.8			

[a] For more structural details, see the footnote of Table 1. [b] $O_1C_1C_3O_2$ dihedral angle (degrees) in the most stable *trans-β*-dik$^\bullet$ radical.

independent of the OCCO dihedral angle in the most stable *trans*-Hβ-dik compounds. The only exceptions are the Hmeacac molecule for which the planar *cis-β*-dik$^\bullet$ conformation is too much destabilized (47 kJ/mol) with respect to the planar trans conformation and the Hdpm derivative for which the cis conformation is only 10 kJ/mol less stable than the trans species. These two deviations are due to important destabilizing steric effects in the *cis* conformation of Hmeacac and in the trans conformation of Hdpm.

4. Conclusions

The gas-phase thermochemistry of 13 β-diketones was investigated by means of DFT performed at the B3LYP/6-311+G(2d,2p)//B3LYP/6-31G(d) level of theory. The full-optimized structures obtained with the larger basis set were compared, whenever possible, with those coming from the most recent experimental works. Generally, the computed values are in excellent agreement with experiment; an important difference between theory and experiment is found for the location of the enol hydrogen atom. In all compounds studied here, the hydrogen atom is preferentially bonded to one of the oxygens. Preference for a perfect or quasi C_{2v} symmetry was not found.

The calculations show that the enol form is stabilized with respect to the keto form if large or electron deficient substituents are attached to the $R_1C(OH)CR_3C(O)R_2$ moiety. Furthermore, C−H rather than O−H bond dissociation enthalpy is much more favorable when R_1 or R_2 or R_3 are of $-CHR_4$ type, such as $-CH_3$ or $-CH(CH_3)_2$. Importantly, it was found that C−H bond homolysis at the $R_3 = -CH_3$ group is a few kJ/mol easier than O−H bond scission or C−H bond cleavage at the lateral $R_1 = -CHR_4$ substituent.

Gas-phase enthalpies estimated for the β-diketones from a substitution working reaction are found to be in rather good agreement with experimentally determined values. Larger differences may be attributed to experimental difficulties in the definition of the tautomeric form of the compound studied, i.e., if it was in an enol or in a keto conformation. Gas-phase enthalpies were also estimated for the most stable β-dik$^\bullet$ radicals. Comparison with experimental results is not possible, but for the smaller acac$^\bullet$ species, the DFT estimated value is almost identical to that coming from CBS-QB3 and CBS-QB3-tz computations and based on several reactions giving enhanced confidence for the other estimates herewith included.

Finally, because these compounds are important ligands for the complexation of metals and because they usually coordinate metals through their *cis*-orientated oxygen atoms, the enthalpy required to rotate the compounds from their most stable distorted-*cis* or distorted-*trans* conformations were also calculated. Furthermore, the energetic profile for the proton transfer from the enol radical to the keto radical of acac$^\bullet$ was also calculated.

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Supporting Information Available: Cartesian coordinates for all Hβ-dik and their derivatives and other molecules used to estimate standard enthalpies of formation of the Hβ-dik compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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