

Energetics of metal-oxygen bonds in metal complexes of β -diketones

Manuel A. V. Ribeiro da Silva and Maria Luisa C. C. H. Ferrão

Chemistry Department, Faculty of Sciences, University of Porto, 4000 Porto, PORTUGAL

Abstract - The thermochemical data available for standard enthalpies of formation, both in the crystalline and gaseous phases, of metal β -diketonates is reviewed, and the calculation of enthalpies of gas-phase decomposition of these complexes is presented. The homolytic metal-oxygen bond-dissociation enthalpies for several complexes of β -diketones with different metals are calculated, and the results discussed in terms of structure and bonding and, whenever appropriate, trends in the data are suggested and discussed.

INTRODUCTION

The β -diketones are generally bidentate ligands which appear to form complexes with virtually all of the nonradioactive metallic and metalloidal elements in the periodic table. Since the preparation of acetylacetonone (2,4-pentanedione) and similar β -dicarbonyl compounds in the later half of last century, chemists have shown considerable interest in their properties and reactions. The presence of β -carbonyl groups with at least one proton on the intermediate carbon atom, allows a tautomeric equilibrium of the keto and enol forms, which is the most important feature of β -diketones, since it is the enolate anion which forms complexes with metals (Fig. 1).

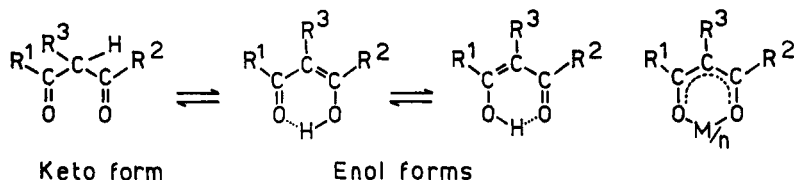


Fig.1. Tautomerism of β -diketones and metal complex formation

β -diketones are weak acids; the 3-proton can easily be lost to give the enolate anion, with a five-atom π network extending over the two oxygens and three non-terminal carbon atoms. Hence, six electrons occupy the resulting π -type molecular orbitals, the enolate anion having a delocalized symmetric structure.

Metal β -diketonates were known as early as 1887, but the nature of the coordinate bond was not completely understood until 1945, when aromaticity within the diketonate ring was suggested. Many metal β -diketonates were rapidly recognized as inner sphere complexes and several such complexes were shown to be volatile, and soluble in organic solvents. The volatility property has been extensively studied in the context of the separation of metals by gas chromatography, and the solubility in organic solvents has been used for solvent extraction of these complexes.

Besides the usual bidentate way of bonding to the metals, through the two oxygen atoms, forming a chelate ring, the β -diketones can be monodentate, and also bridge metal atoms in a number of different ways (ref. 1). Crystallographic studies (ref. 2) for numerous octahedral acetylacetonate complexes show that all coordinated enolate anions have the same symmetry, and that in each complex the six M-O bond distances are equal, within the experimental error.

Coordination compounds involving β -diketones are widely covered in the literature, and various aspects of the structure, bonding and other properties have been treated in several review articles (ref. 3-13), thus certainly reflecting the increasing importance of this field.

The strengths of bonds between transition metals and ligands are of interest because not only of their involvement in biological processes, but the separation, purification of metals and in the catalysis of reactions. Enthalpies of gas-phase reactions of the complexes are necessary to calculate dissociation energies of metal-ligand bonds.

Thermodynamic data for metal β -diketonate complexes were first published in 1953 in the form of stability constant data for these complexes, in aqueous solution.

The thermochemical study of metal β -diketonates began in 1962 when the combustion enthalpy of the majority of the first row transition metal acetylacetonate complexes was reported. This was pioneering work in that these data were used to derive thermochemical homolytic and heterolytic bond-dissociation enthalpies, the later ones being used to show a classical double periodic variation with the atomic number of the metal, as predicted by the simple crystal field theory. The experimental work involved has subsequently been shown to be of very low accuracy, but calculations remain the principal method in use for the derivation of the mean metal-ligand bond-dissociation enthalpies. Since then the thermochemistry of both β -diketones and metal β -diketonate complexes has been progressively and extensively investigated over the last two decades. More thermochemical data are available for metal β -diketonate complexes than for any other group of complexes containing metal-oxygen coordinate bonds. Thus it is possible to classify such thermochemical data into well defined categories and to identify several trends within each category.

Since a wide variety of substituents can be introduced at positions R_1 , R_2 or R_3 of the β -diketone molecule (Fig. 1), it is desirable to use abbreviations for some of the various β -ketoenolates which have been extensively studied. A unique system of abbreviations has not yet been agreed on, and consequently the same compound appears in the literature under different abbreviations. Throughout this paper, the β -diketones will be generally abbreviated as "H β dik", "H" being the enolic hydrogen atom, and " β dik" the abbreviation for the rest of the structure. The abbreviations used are mentioned in Table 1, together with their trivial names.

THERMOCHEMISTRY OF METAL β -DIKETONATES

The calculation of the bond strengths between the metal atoms and ligands requires the knowledge of several thermodynamic parameters for both metal complexes and ligands.

In the case of metal β -diketonates, it is necessary to know the standard enthalpies of formation and of vaporization (sublimation) of the ligands, the molar enthalpy of the dissociation of the enolic hydrogen of the ligands, $\langle D \rangle(\text{O-H, enol, g})$



the standard enthalpy of formation of the metals in the gaseous phase, as well as the standard enthalpies of formation of the crystalline complexes and their standard enthalpies of sublimation.

THERMODYNAMIC PARAMETERS OF β -DIKETONES

The standard enthalpies of formation of β -diketones are of key importance in determining the standard enthalpies of formation of metal β -diketonate complexes from reaction calorimetric studies. The literature mentions experimental values for the standard enthalpies of formation of several β -diketones, determined by precise combustion calorimetry. However, there are no experimental values for the standard enthalpies of formation of trifluoroacetylacetone and hexafluoroacetylacetone to be found, but these values can be estimated on the basis of the existing experimental data for other compounds, by using a Group Scheme. The available, experimental and estimated, data has been recently reviewed (ref. 14).

The available literature values for the standard enthalpies of vaporization of liquid β -diketones, have been measured by a direct calorimetric method, using the Wadsö vaporization calorimeter (ref. 15). For crystalline β -diketones, standard enthalpies of sublimation have also been measured by several different experimental methods. The available values for both vaporization and sublimation enthalpies have also been reviewed recently (ref. 14).

There are no measured values for the molar enthalpy of dissociation of the enolic hydrogen from β -diketones. Several estimates have been made, based on different approaches, and in the literature there are values ranging from 365 kJ mol⁻¹ (ref. 16) to 418 kJ mol⁻¹ (ref. 17). This situation has also been reviewed (ref. 14) and, in this work, for comparison reasons, all the results have been recalculated using $\langle D \rangle(\text{O-H, enol, g}) = 418 \pm 20$ kJ mol⁻¹.

TABLE 1. Nomenclature and abbreviations of β -diketones

| Formula* | Trivial name | Abbreviation |
|--|---------------------------|--------------|
| $\text{CH}_3\text{COCH}_2\text{COCH}_3$ | Acetylacetone | Hacac |
| $\text{CF}_3\text{COCH}_2\text{COCH}_3$ | Trifluoroacetylacetone | Htfac |
| $\text{CF}_3\text{COCH}_2\text{COCF}_3$ | Hexafluoroacetylacetone | Hhfac |
| $(\text{CH}_3)_2\text{CHCOCH}_2\text{COCH}(\text{CH}_3)_2$ | Diisobutyrylmethane | Hdibm |
| $(\text{CH}_3)_3\text{CCOCH}_2\text{COCH}_2\text{CH}_3$ | Pivaloylpropionylmethane | Hpiprm |
| $(\text{CH}_3)_3\text{CCOCH}_2\text{COCH}(\text{CH}_3)_2$ | Isobutyrylpivaloylmethane | Hibpm |
| $(\text{CH}_3)_2\text{CCOCH}_2\text{COC}(\text{CH}_3)_2$ | Dipivaloylmethane | Hdpm |
| $\text{C}_6\text{H}_5\text{COCH}_2\text{COCH}_3$ | Benzoylacetone | Hbzac |
| $\text{C}_6\text{H}_5\text{COCH}_2\text{COC}_6\text{H}_5$ | Dibenzoylmethane | Hdbzm |

*Expressed as the keto form

TABLE 2. Standard enthalpies of formation of β -diketonates and tropolonates of Cu(II), Be(II), Al(III)

| Ligand | $\Delta H_f^\circ(\text{c}) / \text{kJ mol}^{-1}$ | | |
|---------|---|---------------------|---------------------|
| | Cu(II) | Be(II) | Al(III) |
| Hacac | -809.9 ± 1.5^a | -1236.4 ± 2.3^b | -1797.8 ± 3.7^c |
| Htfac | -784.8 ± 2.2^d | | -1793.3 ± 2.0^e |
| Hhfac | -2064 ± 10^f | -2498 ± 10^g | -3696 ± 15^h |
| Hdibm | -3311 ± 10^i | | |
| Hpiprm | -998.0 ± 4.4^j | | |
| Hibpm | -995.5 ± 4.7^k | | |
| Hdpm | -1078.5 ± 4.4^l | | |
| Hbzac | -1111.5 ± 7.8^m | -1552.0 ± 7.8^n | -2255 ± 12^o |
| Hdbzm | -591.4 ± 5.8^p | -1013.1 ± 5.7^q | -1483.6 ± 8.9^r |
| Htrop | -414.8 ± 1.8^s | -855.2 ± 1.8^t | -1262.7 ± 2.8^u |
| HMetrop | | | -1316.7 ± 9.2^v |

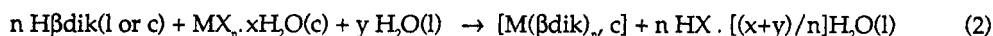
a=Ref. 29 b=Ref. 30 c=Ref. 17 d=Ref. 31 e=Ref. 16
 f=Ref. 32 g=Ref. 33 h=Ref. 34 i=Ref. 35 j=Ref. 36
 k=Ref. 37 l=Ref. 38

STANDARD ENTHALPIES OF FORMATION OF CRYSTALLINE METAL β -DIKETONATE COMPLEXES

The first reported values for the standard enthalpies of formation of metal β -diketonates were obtained by static bomb calorimetry in the early sixties. Jones and co-workers reported the first values for the acetylacetonates of Cu(II) (ref. 18), Ni(II) (ref. 19), Sc(III), V(III), Cr(III), Mn(III), Fe(III), Co(III) (ref. 20) as well as for Fe(bzac)₃ and Fe(dbzm)₃ (ref. 21); Kawasaki, also reported the standard enthalpy of formation of Al(acac)₃ (ref. 22). The experimental work involved has later been shown to be of very low accuracy (ref. 23), probably because insufficient attention was paid to controlling the combustion with auxiliary aids and mainly in defining the completeness of the combustion and the nature of the combustion products.

In 1966, Irving (ref. 17) published the first paper on the determination of the standard enthalpy of formation of a crystalline metal β -diketonate, Al(acac)₃, by solution and reaction calorimetry. Metal β -diketonates, M(β dik)₃ and M(β dik)₂, decompose into metal and free ligand in sulphuric, hydrochloric or perchloric acid, although complexes of low water solubility react slowly; for these particular complexes the rate of reaction can be increased by using a mixture of acid and 1,4-dioxan.

The standard enthalpies of formation of metal β -diketonates, M(β dik)_n, are obtained from the enthalpy change (ΔH_r) which occurs as a result of the reaction (2)



The enthalpy change of the reaction, ΔH_r , is measured indirectly in an isothermally jacketed solution calorimeter by reaction in a non-volatile solvent, in which all the components are soluble. If equilibrium is rapidly reached from either side, the difference between the enthalpies of solution of all products and reactants, in the required stoichiometric ratio, gives the enthalpy of the reaction. The method introduced by Irving has since been used by different workers for measuring standard enthalpies of formation of a great number of crystalline metal β -diketonates, using appropriate solvents.

Cavell and Pilcher (ref. 23), in 1977, measured the enthalpies of combustion and derived the standard enthalpies of formation, of tris(acetylacetonate) of Al(III) ($-1793.3 \pm 2.0 \text{ kJ mol}^{-1}$), Ga(III) ($-1476.0 \pm 4.5 \text{ kJ mol}^{-1}$) and In(III) ($-1405.7 \pm 3.6 \text{ kJ mol}^{-1}$), by static combustion calorimetry, in good agreement with the values derived from reaction calorimetry by Irving *et al.* for Al(III), $-1797.8 \pm 3.7 \text{ kJ mol}^{-1}$ (ref. 17) and Ga(III), $-1487.5 \pm 5.2 \text{ kJ mol}^{-1}$ (ref. 24), thus giving confidence in the reaction calorimetric method.

The modern available values for standard enthalpies of formation of crystalline metal β -diketonates, are summarized in Table 2 [Cu(II), Be(II), Al(III)], Table 3 [Mn(II), Fe(II), Co(II), Ni(II)], Table 4 [Cr(III), Mn(III), Fe(III), Co(III)], and Table 5 (acetylacetonates of Group II metals).

There are also published values for the standard enthalpies of formation of the following crystalline metal β -diketonates: $\Delta H_f^\circ[\text{Pd}(\text{acac})_2, \text{c}] = -756.9 \pm 13 \text{ kJ mol}^{-1}$ (ref. 25), $\Delta H_f^\circ[\text{Pt}(\text{acac})_2, \text{c}] = -687 \pm 5 \text{ kJ mol}^{-1}$ (ref. 26), $\Delta H_f^\circ[\text{Mo}(\text{acac})_3, \text{c}] = -1321.9 \pm 5.9 \text{ kJ mol}^{-1}$ (ref. 27), $\Delta H_f^\circ[\text{V}(\text{acac})_3, \text{c}] = -1522.8 \pm 4.5 \text{ kJ mol}^{-1}$ (ref. 28) and $\Delta H_f^\circ[\text{VO}(\text{acac})_2, \text{c}] = -1366.6 \pm 7.6 \text{ kJ mol}^{-1}$ (ref. 28).

Some of the values reported in this paper, both for the standard enthalpies of formation of the crystalline metal β -diketonate complexes and for the calculated mean metal-oxygen bond-dissociation enthalpies, were recalculated from the original papers reporting the experimental work, using more modern auxiliary data, specially new values for the standard enthalpies of formation of the ligands and for the standard enthalpies of sublimation of the metal β -diketonate complexes.

TABLE 3. Standard enthalpies of formation of $M(\beta\text{dik})_2$, $M(\text{II}) = \text{Mn}(\text{II}), \text{Fe}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II})$

| H β dik | $\Delta H_f^\circ(\text{c}) / \text{kJ mol}^{-1}$ | | | |
|---------------|---|---------------------|--|--|
| | Mn(II) | Fe(II) | Co(II) | Ni(II) |
| Hacac | -1048.1 ± 2.2^a | -946.9 ± 2.2^a | -884.1 ± 2.1^a -868.0 ± 3.0^b | -910.6 ± 2.1^a -861.0 ± 2.1^c -861.0 ± 5.0^d |
| Htfac | $-2609 \pm 10^{*}$ | | -2138 ± 10^e | |
| Hhfac | $-4163 \pm 10^{**}$ | | $-4009 \pm 10^{**}$ | $-4003 \pm 10^{**}$ |
| Hdpm | -1325.7 ± 7.6^f | -1325.7 ± 7.6^f | -1213.3 ± 7.6^f | -1176.7 ± 7.8^c |
| Hbzac | | | -631.2 ± 6.0^g | -631.8 ± 5.8^h -658.6 ± 4.2^b |

* This value is for $\Delta H_f^\circ [\text{Mn}(\text{tfac})_2 \cdot \text{H}_2\text{O}]$

** These values are for $\Delta H_f^\circ [\text{M}(\text{hfac})_2 \cdot (\text{H}_2\text{O})_2]$

a=Ref. 31 b=Ref. 39 c=Ref. 40 d=Ref. 25 e=Ref. 41 f=Ref. 42 g=Ref. 43 h=Ref. 44

TABLE 4. Standard enthalpies of formation of $M(\beta\text{dik})_3$, $M(\text{III}) = \text{Cr}(\text{III}), \text{Mn}(\text{III}), \text{Fe}(\text{III}), \text{Co}(\text{III})$

| H β dik | $\Delta H_f^\circ(\text{c}) / \text{kJ mol}^{-1}$ | | | |
|---------------|---|---------------------|---------------------|--------------------|
| | Cr(III) | Mn(III) | Fe(III) | Co(III) |
| Hacac | -1564.8 ± 8.9^a | -1379.0 ± 3.7^b | -1314.7 ± 3.0^c | |
| Htfac | -3486 ± 17^d | | -3220 ± 15^e | -3191 ± 15^f |
| Hhfac | -5471 ± 17^d | | -5115 ± 15^e | |
| Hdpm | -1977 ± 14^d | -1863 ± 12^g | -1813 ± 12^e | -1708 ± 12^f |
| Hbzac | -1185 ± 12^d | -1044.9 ± 8.8^g | -985.2 ± 8.5^e | -877.2 ± 8.7^f |

a=Ref. 45 b=Ref. 46 c=Ref. 47 d=Ref. 48 e=Ref. 49 f=Ref. 50 g=Ref. 41

TABLE 5. Standard enthalpies of formation of acetylacetonates of the Group II metals

| $\Delta H_f^\circ[\text{M}(\text{acac})_2, \text{c}] / \text{kJ mol}^{-1}$ | | | | |
|--|---------------------|--|---------------------|---------------------|
| Be | Mg | Ca | Sr | Ba |
| -1236.4 ± 2.3^a | -1263.2 ± 2.2^a | -1348.9 ± 2.4^a -1323.1 ± 2.2^b | -1344.9 ± 3.1^a | -1332.9 ± 3.1^a |
| | | Zn | Cd | Hg |
| | | -961.8 ± 3.0^a -949.9 ± 2.2^b -849.9 ± 6.9^c | -903.1 ± 2.4^a | -723.9 ± 2.7^a |

a=Ref. 30 b=Ref. 31 c=Ref. 51

STANDARD ENTHALPIES OF SUBLIMATION OF METAL β -DIKETONATES

The standard enthalpies of sublimation of coordination compounds are of key importance, since it is necessary to refer the standard enthalpies of formation to the ideal gas state in order to remove the intermolecular forces, and so calculate the strengths of the coordinated bonds.

The great majority of coordination compounds are not appreciably volatile at the standard temperature and pressure and so specialized techniques are required which involve high vacuum apparatus operating at high temperatures (ref. 52).

Several methods have been used to measure enthalpies of sublimation of metal β -diketonates, but unfortunately the values derived for the same complex by different techniques are generally inconsistent, so that large discrepancies exist between reported enthalpies of sublimation for metal β -diketonate complexes. For example, there are nine different values published for $\Delta H_{\text{sub}}^{\circ}[\text{Fe}(\text{acac})_3, \text{c}]$, ranging from 19 kJ mol⁻¹ (ref. 53), obtained by the isotenoscopic method by Berg and Truemper, to 121 kJ mol⁻¹ (ref. 54), obtained by the sublimation bulb technique. A similar situation can be found for most of the other metal β -diketonates, showing that this area is widely open for further research.

In view of the present situation, it is necessary to choose sensible values among those published so far. Under these circumstances, where a choice is available, we have preferred to select a value obtained by the Knudsen effusion techniques or by the direct "vacuum sublimation drop microcalorimetric method" of Skinner *et al.* (ref. 55). Although this later method is a simple and easy one, it yields results that appear to be reliable to ± 4 kJ mol⁻¹ (ref. 56). Where no experimental values for the enthalpy of sublimation are available, they have to be estimated on the basis of structure, physical properties and of other known trends (ref. 14). The selected values used for the calculations of the present work are either those registered on Table 6 or those which the authors of several reference papers have used in their own calculations.

TABLE 6. Standard enthalpies of sublimation of metal β -diketonates

| Ligand | $\Delta H_{\text{sub}}^{\circ} / \text{kJ mol}^{-1}$ | | | | | |
|--------|--|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| | Cr(III) | Fe(III) | Co(III) | Cu(II) | Be(II) | Al(III) |
| Hacac | ^a 123 \pm 3 | | | ^b 110 \pm 4 | ^a 94 \pm 1 | ^a 120 \pm 3 |
| Htfac | ^a 117 \pm 4 | ^a 138 \pm 4 | ^f 114 \pm 4 | ^a 112 \pm 3 | ^a 88 \pm 4 | ^a 108 \pm 2 |
| Hhfac | ^a 112 \pm 4 | | | ^a 108 \pm 6 | | |
| Hdibm | | | | ^b 118 \pm 4 | | |
| Hpiprm | | | | ^b 123 \pm 4 | | |
| Hibpm | | | | ^b 126 \pm 4 | | |
| Hdpm | ^a 133 \pm 4 | ^c 146 \pm 4 | ^f 126 \pm 4 | ^b 123 \pm 7 | ^a 102 \pm 3 | ^a 119 \pm 3 |
| Hbzac | ^a 186 \pm 4 | ^c 200 \pm 4 | | ^b 160 \pm 4 | ^c 142 \pm 4 | ^c 194 \pm 4 |

^aMeasured by the Knudsen Technique

^bMeasured by the Vacuum Sublimation Drop Technique (ref. 55)

a=Ref. 57 b=Ref. 29 c=Ref. 36 d=Ref. 48 e=Ref. 49 f=Ref. 50

THE MEAN METAL-OXYGEN BOND-DISSOCIATION ENTHALPIES

From the standard enthalpies of formation of crystalline metal β -diketonates, $\Delta H_f^{\circ}[M(\beta\text{-dik})_n, \text{c}]$, and the corresponding standard enthalpies of sublimation, $\Delta H_{\text{sub}}^{\circ}[M(\beta\text{dik})_n, \text{c}]$, the standard enthalpies of formation of the gaseous metal β -diketonates, $\Delta H_f^{\circ}[M(\beta\text{dik})_n, \text{g}]$ can be derived.

The mean metal-oxygen homolytic bond-dissociation enthalpies, $\langle D \rangle(\text{M-O})$, can be derived from the molar enthalpies of dissociation, $\Delta H_{\text{d}}^{\circ}$, of the hypothetical dissociation reaction of the gaseous molecules into metal atoms and ligand radicals



Since the oxygen atoms in metal β -diketonates are equivalent (ref. 2), the $\langle D \rangle$ (M-O) values are calculated as

$$\langle D \rangle(M-O) = \Delta H_{rx} / 2n \quad (4)$$

with

$$\Delta H_{rx} = \Delta H_f^\circ(M, g) + n \Delta H_f^\circ(H\beta dik, g) - n \Delta H_f^\circ(H, g) - \Delta H_f^\circ[M(\beta dik)_n, g] + n \langle D \rangle(O-H, enol, g) \quad (5)$$

where $\langle D \rangle$ (O-H, enol, g), the molar enthalpy of dissociation of the enolic hydrogen of the ligands, defined by equation 1, is taken as 418 ± 20 kJ mol⁻¹ for all the β -diketones, as discussed before, and as 376 ± 20 kJ mol⁻¹ for tropolone and 4-methyltropolone (ref. 38).

The mean metal-oxygen bond-dissociation enthalpies for the metal β -diketonates have been calculated and summarized in Tables 7, 8 and 9.

TABLE 7. Mean metal-oxygen bond-dissociation enthalpies in M(β -dik),

| H β dik | $\langle D \rangle$ (M-O) / kJ mol ⁻¹ | | | | | |
|---------------|--|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| | Be(II) | Mn(II) | Fe(II) | Co(II) | Ni(II) | Cu(II) |
| Hacac | 274 \pm 10 ^a | 218 \pm 10 ^d | 219 \pm 10 ^d | 202 \pm 11 ^e | 202 \pm 10 ^b | 167 \pm 10 ^j |
| Hbzac | 273 \pm 10 ^b | | | 201 \pm 10 ^e | 203 \pm 11 ⁱ | 167 \pm 10 ^k |
| Htfac | 277 \pm 11 ^c | 212 \pm 11 ^e | | 206 \pm 11 ^e | | 165 \pm 11 ^l |
| Hhfac | | 217 \pm 11 ^e | | 203 \pm 11 ^e | 203 \pm 11 ^e | 164 \pm 11 ^l |
| Hdpm | 280 \pm 10 ^c | 201 \pm 10 ^f | 235 \pm 12 ^f | 209 \pm 11 ^f | 202 \pm 11 ^b | 168 \pm 10 ^j |
| Hdibm | | | | | | 169 \pm 10 ^j |
| Hpiprm | | | | | | 168 \pm 10 ^j |
| Hibpm | | | | | | 168 \pm 10 ^j |
| Htrop | 272 \pm 12 ^c | | | | | 155 \pm 10 ^m |
| Average | 275 | 212 | 227 | 204 | 203 | 166 |

a=Ref. 30 b=Ref. 36 c=Ref. 33 d=Ref. 31 e=Ref. 41 f=Ref. 42 g=Ref. 39 h=Ref. 40
i=Ref. 43 j=Ref. 29 k=Ref. 35 l=Ref. 32 m=Ref. 37

TABLE 8. Mean metal-oxygen bond-dissociation enthalpies in M(β dik),

| H β dik | $\langle D \rangle$ (M-O) / kJ mol ⁻¹ | | | | |
|---------------|--|---------------------------|---------------------------|---------------------------|---------------------------|
| | Cr(III) | Mn(III) | Fe(III) | Co(III) | Al(III) |
| Hacac | 214 \pm 10 ^a | 165 \pm 10 ^c | 174 \pm 10 ^e | | 243 \pm 10 ^h |
| Hbzac | 207 \pm 11 ^b | 163 \pm 10 ^d | 175 \pm 10 ^f | 164 \pm 10 ^g | 244 \pm 10 ⁱ |
| Htfac | 221 \pm 11 ^b | | 176 \pm 11 ^f | 177 \pm 10 ^g | 246 \pm 10 ^j |
| Hhfac | 238 \pm 11 ^b | | 180 \pm 11 ^f | | |
| Hdpm | 209 \pm 10 ^b | 170 \pm 10 ^d | 183 \pm 10 ^f | 171 \pm 10 ^g | 247 \pm 10 ^j |
| Htrop | | | | | 246 \pm 12 ^k |
| HMetrop | | | | | 238 \pm 12 ^k |
| Average | 218 | 166 | 178 | 171 | 244 |

a=Ref. 45 b=Ref. 48 c=Ref. 46 d=Ref. 41 e=Ref. 47 f=Ref. 49 g=Ref. 50 h=Ref. 17
i=Ref. 36 j=Ref. 34 k=Ref. 38

TABLE 9. Mean metal-oxygen bond-dissociation enthalpies in Group II metal acetylacetonates

| $\langle D \rangle(\text{M-O}) / \text{kJ mol}^{-1}$ (ref. 30) | | | | |
|--|--------------|--------------|--------------|--------------|
| Be | Mg | Ca | Sr | Ba |
| 274 ± 10 | 230 ± 10 | 255 ± 10 | 245 ± 10 | 241 ± 10 |
| | | Zn | Cd | Hg |
| | | 148 ± 10 | 128 ± 10 | 71 ± 10 |

TABLE 10. Derived standard molar values (in kJ mol^{-1}) at 298.15 K for metal(II) oxides

| M | $\Delta H_f^\circ(\text{M}, \text{g})$ | $\Delta H_f^\circ(\text{MO}, \text{g})$ | $D(\text{M-O})_g$ | $\Delta H_f^\circ(\text{MO}, \text{c})$ | $D(\text{M-O})_c$ |
|----|--|---|-------------------|---|-------------------|
| Be | 324 ± 5^a | 117^b | 456 | -609.2 ± 2.5^b | 296 |
| Mg | 147.1 ± 0.8^a | 17^b | 379 | -601.5 ± 0.3^b | 250 |
| Ca | 177.8 ± 0.8^a | | | -635.1 ± 1.0^b | 266 |
| Sr | 163.6 ± 4.2^a | -8^b | 421 | -590.5 ± 1.0^b | 251 |
| Ba | 177.8 ± 4.2^a | -117^b | 544 | -548.1 ± 2.1^b | 244 |
| Zn | 130.4 ± 0.2^a | | | -350.6 ± 0.3^b | 183 |
| Cd | 110.0 ± 0.4^a | | | -259.0 ± 1.3^b | 155 |
| Hg | 61.4 ± 0.1^a | | | -90.8 ± 0.1^b | 100 |
| Mn | 280.7 ± 4.2^c | 124.2 ± 4.2^c | 404 | -385.2 ± 4.2^c | 228 |
| Co | 424.7 ± 4.2^c | 309.4^d | 365 | -237.9 ± 0.5^c | 228 |
| Ni | 429.7 ± 4.2^c | 314^c | 366 | -239.7 ± 4.2^c | 230 |
| Cu | 337.6 ± 1.2^c | 320.0^d | 267 | -157.3 ± 4.2^c | 186 |
| Pd | 378.2 ± 4.2^c | 348.9 ± 4.2^c | 278 | -85.4 ± 4.2^c | 178 |

$D(\text{M-O})_g = \langle D \rangle(\text{M-O}, \text{oxide}, \text{g})$ $D(\text{M-O})_c = \langle D \rangle(\text{M-O}, \text{oxide}, \text{c})$
 a=Ref. 58 b=Ref. 59 c=Ref. 60 d=Ref. 61

Other calculated values for acetylacetonate complexes are as follows: $\langle D \rangle(\text{Pd-O}) = 159 \pm 11 \text{ kJ mol}^{-1}$ (ref. 25), $\langle D \rangle(\text{Pt-O}) = 193 \pm 10 \text{ kJ mol}^{-1}$ (ref. 26), $\langle D \rangle(\text{Ga-O}) = 184 \pm 10 \text{ kJ mol}^{-1}$ (ref. 24), $\langle D \rangle(\text{In-O}) = 162 \pm 10 \text{ kJ mol}^{-1}$ (ref. 23), $\langle D \rangle(\text{Mo-O}) = 218 \pm 10 \text{ kJ mol}^{-1}$ (ref. 27), $\langle D \rangle(\text{V-O}) = 227 \pm 10 \text{ kJ mol}^{-1}$ (ref. 28) and $\langle D \rangle(\text{VO-O}) = 252 \pm 10 \text{ kJ mol}^{-1}$ (ref. 28).

The available results allow several conclusions to be drawn. From Tables 7 and 8, it is clear that the mean metal-oxygen bond-dissociation enthalpies, for the same metal with different ligands, are almost the same within the associated uncertainties; the average values of $\langle D \rangle(\text{M-O})$ for the same metal are shown in last rows of the tables. These almost constant values for $\langle D \rangle(\text{M-O})$ suggest that, for a certain metal, the mean metal-oxygen bond-dissociation enthalpy is not affected by the structure of the ligand, and so, as the metal is completely surrounded by the oxygens atoms of the ligands, it must be totally oxidized, *i. e.*, in an oxidation state similar to the one of the corresponding metal-oxide. So, a linear correlation $\langle D \rangle(\text{M-O}, \text{complex}, \text{g}) = f \{ \langle D \rangle(\text{M-O}, \text{oxide}, \text{g}) \}$ is to be expected, where $\langle D \rangle(\text{M-O}, \text{oxide}, \text{g})$ is the enthalpy of dissociation ($\Delta H_{\text{diss}}^\circ$) for the reaction



This can be only tested for metals with oxidation number two, since there are no published values for $\Delta H_f^\circ(\text{M}_2\text{O}_3, \text{g})$. Table 10 lists the values of $\Delta H_f^\circ(\text{M}, \text{g})$, $\Delta H_f^\circ(\text{MO}, \text{g})$, and the calculated $\langle D \rangle(\text{M-O}, \text{oxide}, \text{g})$. The observed correlation is depicted in Fig. 2 and it is excellent for transition metals, but not satisfactory for the group II metals (alkaline earths), probably due to their highly ionized structure or the available values for $\Delta H_f^\circ(\text{MO}, \text{g})$.

It might also be expected (ref. 14) that the metal-oxygen bonds in metal β -diketonates are more similar to the corresponding bonds of the crystalline oxides, since, in the oxides with polymeric structures, the metal has a coordination number and a configuration equal to the one in the complexes. Then, from the molar enthalpy of decomposition (ΔH_{dec}°)



a parameter may be defined,

$$\langle D \rangle (M-O, \text{oxide}, c) = \Delta H_{dec}^\circ / \text{coord. number of metal} \quad (8)$$

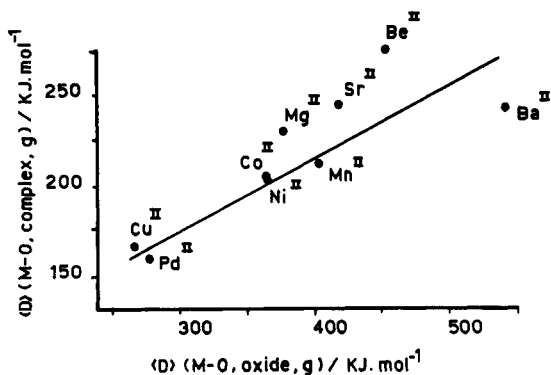


Fig. 2. Variation of $\langle D \rangle$ [M(II)-O, complex, g] with $\langle D \rangle$ [M(II)-O, oxide, g]

TABLE 11. Derived standard molar values (in kJ mol^{-1}) at 298.15 K for metal(III) oxides

| M | $\Delta H_f^\circ(M, g)^a$ | $\Delta H_f^\circ(M_2O_3, c)^a$ | $D(M-O)_c$ |
|----|----------------------------|---------------------------------|------------|
| Cr | 396.6 ± 4.2 | -1139.7 ± 4.2 | 447 |
| V | 514.2 ± 4.2 | -1218.8 ± 4.2 | 499 |
| Mn | 280.7 ± 4.2 | -959.0 ± 4.2 | 377 |
| Al | 326.4 ± 4.2 | -1675.7 ± 4.2 | 514 |
| Ga | 277.0 ± 4.2 | -1089.1 ± 4.2 | 398 |
| In | 243.3 ± 4.2 | -925.8 ± 4.2 | 360 |
| Fe | 416.3 ± 4.2 | -824.2 ± 4.2 | 401 |

a=Ref. 60

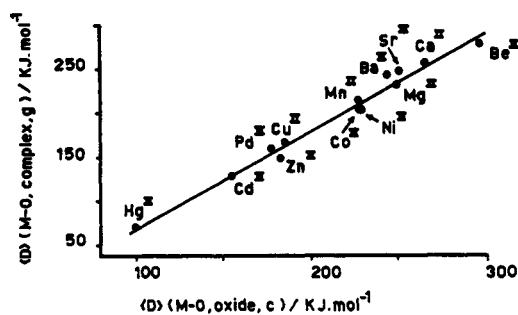


Fig. 3. Variation of $\langle D \rangle$ [M(II)-O, complex, g] with $\langle D \rangle$ [M(II)-O, oxide, c].

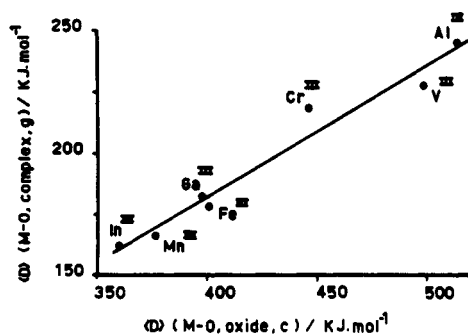


Fig. 4. Variation of $\langle D \rangle$ [M(III)-O, complex, g] with $\langle D \rangle$ [M(III)-O, oxide, c].

Tables 10 and 11 provide the necessary data to establish these correlations. The correlation between $\langle D \rangle (M-O, \text{complex}, g)$ and $\langle D \rangle (M-O, \text{oxide}, c)$, shown in Fig. 3 for $M(\beta\text{dik})_2$ is excellent, although this empirical correlation is approximate owing to the uncertainties in the estimates of $\Delta H_{dec}^\circ [M(\beta\text{dik})_n, c]$ and because not all the oxides are isomorphous: all have rock-salt structures except BeO and ZnO which have wurtzite structures. The structure adopted by the oxide is dependent on the ionic radius ratios and since the energy difference between rock-salt and wurtzite structures is not expected to be large, it should have only a minor influence on the appropriate value to be selected for $\langle D \rangle (M-O, \text{oxide}, c)$. A similar correlation for $M(\beta\text{dik})_3$, shown in Fig. 4, is also excellent. In this case, all the oxides have the $\alpha\text{-Al}_2\text{O}_3$ structures, except Mn_2O_3 and In_2O_3 .

If one thinks in terms of interatomic distances, despite the fact that not all of the molecular structures are known, the results seem consistent with the fact that for different β -diketonates of the same metal, the metal-oxygen bond length is almost constant (ref. 2).

The average value for $\langle D \rangle(\text{Cr-O})$ is 218 kJ mol^{-1} (Table 8). For the tris(β -diketonate)chromium(III) complexes whose crystal structures are known (ref. 62 and 63), the average Cr-O bond length is 195.4 pm. Entering this value in the suggested correlation (ref. 64) $\langle D \rangle(\text{Cr-O}) = f(r(\text{Cr-O}))$, one estimates $\langle D \rangle(\text{Cr-O}) = 220 \text{ kJ mol}^{-1}$, in excellent agreement with the experimental value for tris(β -diketonate)chromium(III) complexes.

For the cobalt and manganese β -diketonates, $\langle D \rangle[\text{Co(II)-O}]$ is larger than $\langle D \rangle[\text{Co(III)-O}]$ and $\langle D \rangle[\text{Mn(II)-O}]$ is also larger than $\langle D \rangle[\text{Mn(III)-O}]$, which can be assumed to result from the increase in electronic density of the metal ion (ref. 65).

Some metal β -diketonates are oligomeric in the solid state. For instance the crystal structure of the acetylacetonates of nickel(II) (ref. 66) and cobalt(II) (ref. 67) showed their trimeric and tetrameric nature, respectively.

Some information on the relative strengths of the bridging and non-bridging metal-oxygen bonds can be obtained. For instance, for the tris[bis(pentane-2,4-dionato)nickel(II)], one can calculate the ΔH°_f $\{[\text{Ni}(\text{acac})_2]_3, \text{g}\}$ and subsequently the enthalpy of disruption of reaction (9), $\Delta H_{\text{dis}} = 2481 \text{ kJ mol}^{-1}$



which represents the sum of the 18 (Ni-O) bonds in the trimer:

$$\Delta H_{\text{dis}} = 6 \langle D \rangle(\text{Ni-O})_{\text{term.}} + 12 \langle D \rangle(\text{Ni-O})_{\text{bridg.}} \quad (10)$$

The x-ray structure of $[\text{Ni}(\text{acac})_2]_3$ (ref. 66) shows a Ni-O distance of 201 pm for the terminal (non-bridging) oxygen atoms, and 212 pm for the bridging ones. If the bond-dissociation enthalpy of the terminal bonds is taken as 202 kJ mol^{-1} , as in the monomeric bis(dipivaloylmethanato)nickel(II), the average nickel-oxygen bond-dissociation enthalpy for the bridging bonds is calculated as

$$\langle D \rangle(\text{Ni-O})_{\text{bridg.}} = 106 \text{ kJ mol}^{-1},$$

close to half of that for the terminal nickel-oxygen bonds.

Acknowledgements

We thank NATO (Research Grant 1709), Instituto Nacional de Investigação Científica, Lisboa (Research Project L5, CIQ, U.P.) and Junta Nacional de Investigação Científica e Tecnológica, Lisboa (Research Contract no. 220-80.32) for partial support of this work.

REFERENCES

1. D. W. Thompson, *Structure and Bonding*, **9**, 27 (1972).
2. E. C. Lingafelter and R. L. Braun, *J. Am. Chem. Soc.*, **88**, 2951 (1966).
3. J. P. Fackler, Jr., *Prog. Inorg. Chem.*, **7**, 361 (1961).
4. R. W. Moshier and R. E. Sievers, *Gas Chromatography of Metal Chelates*, Pergamon Press, Oxford (1965).
5. J. P. Collman, *Reactions of Coordinated Ligands*, p. 78, Am. Chem. Soc., Washington (1963).
6. J. P. Collman, *Angew. Chem. Internat. Edit.*, **4**, 132 (1965).
7. B. Bock, K. Flatau, H. Junge, M. Kuhr and H. Musso, *Angew. Chem. Internat. Edit.*, **10**, 225, (1971).
8. J. Selbin, *Chem. Rev.*, **65**, 153 (1965).
9. E. C. Lingafelter, *Coord. Chem. Rev.*, **1**, 151 (1966).
10. F. Bonati, *Organometal. Chem. Rev.*, **1**, 379 (1966).
11. J. J. Fortman, *Coord. Chem. Rev.*, **6**, 331 (1971).
12. K. C. Joshi and V. N. Pathak, *Coord. Chem. Rev.*, **22**, 37 (1977).
13. R. C. Mehrotra, R. Bohra and D. P. Gaur, *Metal β -Diketones and Allied Derivatives*, Academic Press, London (1978).
14. M. A. V. Ribeiro da Silva, editor. *Thermochemistry and Its Applications to Chemical and Biochemical Systems*, p. 317, NATO ASI series, Reidel: Dordrecht (1984).
15. I. Wadsö, *Acta Chem. Scand.*, **20**, 536 (1966).

16. K. J. Cavell and G. Pilcher, *J. Chem. Soc. Faraday I*, **73**, 1590 (1977).
17. J. O. Hill and R. J. Irving, *J. Chem. Soc. (A)*, **1966**, 971.
18. M. M. Jones, B. J. Yow and W. R. May, *Inorg. Chem.*, **1**, 166 (1962).
19. J. L. Wood and M. M. Jones, *J. Phys. Chem.*, **67**, 1049 (1963).
20. J. L. Wood and M. M. Jones, *Inorg. Chem.*, **3**, 1553 (1964).
21. D. T. Farrar and M. M. Jones, *J. Phys. Chem.*, **68**, 1717 (1964).
22. Y. Kawasaki, T. Tanaka and R. Okawara, *Technol. Reports Osaka Univ.*, **13**, 217 (1963).
23. K. J. Cavell and G. Pilcher, *J. Chem. Soc. Faraday Trans. I*, **73**, 1590 (1977).
24. R. J. Irving and G. W. Walter, *J. Chem. Soc. (A)*, **1969**, 2690.
25. P. M. Burkinshaw and C. T. Mortimer, *Thermoch. Acta*, **102**, 109 (1986).
26. G. Al-Takhin, G. Pilcher, J. Bickerton and A. A. Zari, *J. Chem. Soc. Dalton Trans.*, **1983**, 2657.
27. G. Pilcher, K. J. Cavell, C. D. Garner and S. Parkes, *J. Chem. Soc. Dalton Trans.*, **1978**, 1311.
28. E. H. Jamea and G. Pilcher, *Thermoch. Acta*, **97**, 77 (1986).
29. M. A. V. Ribeiro da Silva, M. D. M. C. Ribeiro da Silva, A. P. S. M. C. Carvalho, M. J. Akello and G. Pilcher, *J. Chem. Thermodynamics*, **16**, 137 (1984).
30. M. A. V. Ribeiro da Silva, G. Pilcher and R. J. Irving, *J. Chem. Thermodynamics*, accepted (1987).
31. W. Kakolowicz and E. Giera, *J. Chem. Thermodynamics*, **15**, 203 (1983).
32. M. A. V. Ribeiro da Silva and M. L. C. C. H. Ferrão, *J. Chem. Thermodynamics*, in print.
33. R. J. Irving and M. A. V. Ribeiro da Silva, *J. Chem. Soc. Dalton Trans.*, **1977**, 413.
34. R. J. Irving and M. A. V. Ribeiro da Silva, *J. Chem. Soc. Dalton Trans.*, **1976**, 1940.
35. M. A. V. Ribeiro da Silva and A. M. M. V. Reis, *Bull. Chem. Soc. Jpn.*, **52**, 3080 (1979).
36. M. A. V. Ribeiro da Silva and A. M. M. V. Reis, *J. Chem. Thermodynamics*, **15**, 957 (1983).
37. M. A. V. Ribeiro da Silva and R. J. Irving, *Bull. Chem. Soc. Jpn.*, **50**, 734 (1977).
38. R. J. Irving and M. A. V. Ribeiro da Silva, *J. Chem. Soc. Dalton Trans.*, **1975**, 1257.
39. R. J. Irving and M. A. V. Ribeiro da Silva, *J. Chem. Soc. Dalton Trans.*, **1981**, 99.
40. R. J. Irving and M. A. V. Ribeiro da Silva, *J. Chem. Soc. Dalton Trans.*, **1978**, 399.
41. M. A. V. Ribeiro da Silva and M. L. C. C. H. Ferrão, unpublished results.
42. E. Giera and W. Kakolowicz, *Thermoch. Acta*, **90**, 71 (1985).
43. M. A. V. Ribeiro da Silva and A. M. M. V. Reis, *Thermoch. Acta*, **55**, 89 (1982).
44. W. Kakolowicz and E. Giera, *Thermoch. Acta*, **32**, 19 (1979).
45. J. O. Hill and R. J. Irving, *J. Chem. Soc. (A)*, **1967**, 1413.
46. J. O. Hill and R. J. Irving, *J. Chem. Soc. (A)*, **1968**, 3116.
47. J. O. Hill and R. J. Irving, *J. Chem. Soc. (A)*, **1968**, 1052.
48. M. A. V. Ribeiro da Silva and M. L. C. C. H. Ferrão, *J. Chem. Thermodynamics*, **19**, 645 (1987).
49. M. A. V. Ribeiro da Silva and M. L. C. C. H. Ferrão, *J. Chem. Thermodynamics*, accepted (1987).
50. M. A. V. Ribeiro da Silva and M. L. C. C. H. Ferrão, *Bull. Chem. Soc. Jpn.*, accepted (1987).
51. C. Airolidi, *Thermoch. Acta*, **90**, 343 (1985).
52. H. A. Skinner, *M. T. P. Int. Rev. of Sci., Phys. Chem. Ser. 1*, vol 10, *Thermochem.. Thermodyn.*, Butterworths, London (1972).
53. E. W. Berg and J. T. Truemper, *J. Phys. Chem.*, **64**, 487 (1960).
54. J. Sachinidis and J. O. Hill, *Thermoch. Acta*, **35**, 59 (1980).
55. F. A. Adedeji, D. L. S. Brown, J. A. Connor, M. Leung, M. I. Paz-Andrade and H. A. Skinner, *J. Organometallic Chem.*, **97**, 221 (1975).
56. F. R. Hartley and S. Patai, editors, *The Chemistry of Metal-Carbon Bond*, p. 43, Wiley, New York (1982).
57. H. Naghbi-Bidokhti, *Ph. D. Thesis*, University of Surrey (1977).
58. G. Pilcher and H. A. Skinner, *The Chemistry of Metal-Carbon Bond*, chap. 2, Wiley, New York (1982).
59. V. P. Glusko and V. A. Medvedev, *Thermal Constants of Compounds*, Akad. Nauk. USSR, Moscow (1974).
60. The NBS Tables of Chemical Thermodynamic Properties, *J. Phys. Chem. Ref. Data*, **11**, suppl. no. 2 (1982).
61. V. P. Glusko, editor, *Thermochemical Constants of Chemical Substances*, **6**, Academy of Sciences, USSR, Moscow (1973).
62. B. Morosin, *Acta Cryst.*, **19**, 131 (1978).
63. B. G., Thomas, M. L. Morris and R. L. Hilderbrandt, *Inorg. Chem.*, **17**, 2901 (1978).
64. K. J. Cavell, C. D. Garner, J. A. Martinho Simões, G. Pilcher, H. Al-Samman, H. A. Skinner, G. Al-Tekhin, I. B. Walton and M. T. Zafarani-Moattar, *J. Chem. Soc. Faraday Trans. I*, **77**, 2927 (1981).
65. J. O. Connor, *Topics on Current Chemistry*, **71**, 71 (1977).
66. G. J. Bullen, R. Mason and P. Pauling, *Inorg. Chem.*, **4**, 456 (1965).
67. F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **5**, 1200 (1966).