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Standard enthalpies of formation of sulfosalicilates of calcium, magnesium, zinc and aluminium

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Abstract

Standard enthalpies of formation of sulfosalicylates of calcium, magnesium, zinc and aluminium have been determined by rotating bomb oxygen calorimetry and the mean dissociation enthalpies of the respective M–O bonds have been computed using suitable empirical thermochemical cycles. The homolytic and heterolytic contributions to the mean disruption enthalpies have been calculated and the effect of the introduction of the sulphonyl group into salicylic acid on the dissociation energies has been investigated.

Key words: Rotating bomb calorimetry, combustion, sulfosalicylates, Ca, Mg, Zn and Al, enthalpies of formation, enthalpies of chelation in gaseous and condensed phases, M–O bond, mean-bond dissociation enthalpies

1. Introduction

The techniques of static oxygen bomb calorimetry and reaction calorimetry have been used for the determination of enthalpies of formation and chelation of several inner complexes. This work was initiated by Jones[1] in USA, followed by Pilcher[2] in UK and our laboratory[3,4]. Studies in these fields have established that the mean M–O bond dissociation energies for the same metal with different ligands are more or less constant within the associated uncertainties. da Silva and Reis[5] reported the standard molar enthalpies of formation of bis(benzoylacetonato)beryllium(II) and tris(benzoylacetonato)-aluminium(III) and the mean molar M–O bond dissociation enthalpies. da Silva *et al*[6] have also established that the introduction of a methyl or a phenyl group into a β-diketonato complex does not influence the M–O bond dissociation energies and this may be regarded as applicable to compounds containing these groups. da Silva has reviewed excellently the thermochemistry of β-diketones, substituted β-diketonates and metal β-diketonates in a recent publication[7].

Static bomb calorimetry has been found to be unsuitable for the combustion of compounds containing halogens, sulphur, boron, etc., for want of thermodynamic equilibrium inside the bomb after combustion. Hence, a rotating bomb calorimeter was fabricated in this laboratory following the design of Good *et al*[8].

Salicylic acid, its derivatives and complexes formed by them find many applications in industry[9,10], medicine[11] and analytical chemistry[12]. Among its derivatives, sulphosalicylic acid forms well-defined inner complexes most suitable for the thermochemical studies of compounds containing sulphonic acid group, though not directly bonded to the metal atom. In the present work, the combustion enthalpies of the sulphosalicylates of Al, Ca, Mg and Zn have been determined by rotating bomb oxygen calorimetry and the bond dissociation enthalpies of the M–O bonds computed.

2. Experimental

All the reagents used in this work were of BDH Analar quality unless otherwise specified. The methods of preparation and the analysis of the compounds under study have been reported by Rajagopalan *et al*[13].

Enthalpies of combustion of the compounds were determined in a specially fabricated rotating type of oxygen bomb calorimeter. The temperature rise of the calorimeter was measured with the help of Stantel F-15-type thermistor as one arm of a Wheatstone bridge circuit, the imbalance potential being recorded by means of 0–10 mV self-balancing potentiometric-type recorder. Thermal calibrations were made by the electrical method.

The apparatus was calibrated and tested by measuring the enthalpies of combustion of BCS benzoic acid and sulphur. The enthalpy of combustion of pure rhombic sulphur using this calorimeter with paraffin oil as the ignition aid was found to be $-887.0 \pm 0.4\,\mathrm{kJ\,mole^{-1}}$ for the reaction

$$S(C, rh) + H_2(g) + 2O_2(g) + 115\,H_2O(l) \rightarrow H_2SO_4, 115\,H_2O(l) \qquad (1)$$

as against the reported[14] literature value of $-887.8 \pm 0.3\,\mathrm{kJ\,mole^{-1}}$.

The compounds were made into pellets of 10 mm diameter and 5–8 mm thickness using a hand press and fired by passing a high current through a fuse wire. Ten ml of distilled water was taken in the bomb during the experiment. The bomb was filled with oxygen to a pressure of 30 atmospheres. The nitrogen originally present in the bomb was not removed in order to facilitate the complete conversion of sulphur to sulphuric acid as the oxides of nitrogen formed during the combustion will act as a catalyst. The final bomb solution was analysed for sulphuric and nitric acids; atomic absorption spectroscopy showed that metal ions were absent. Chemical and X-ray analyses were made of the solid oxides as these were produced at high temperatures and hence were insoluble in the bomb solution.

3. Results and discussion

Corrections were applied in each case for the formation of sulphuric and nitric acids in the bomb after combustion. The end products were found to be the respective oxides in all the cases.

Table I lists the thermochemical properties of the compounds, and column 2 in it the experimentally determined heats of combustion after proper corrections[14]. It was estimated

Table I
Thermochemical values of compounds (kJ mole^{-1} at 298 °K)

Compound	ΔH_{comb}	Standard deviation	$-\Delta H°f$	Standard deviation	$\Delta H_{chel(c)}$	$\Delta H_{chel(g)}$
Sulphosalicylic acid dihydrate	2201	3	1982	3	—	—
Alumino sulphosalicylic acid, tetrahydrate	2963	4	2487	4	353	− 98
Calcium sulphosalicylate, dihydrate	2465	4	2068	4	− 81	− 262
Magnesium sulphosalicylate tetrahydrate	2571	2	2500	2	54	− 181
Zinc sulphosalicylate tetrahydrate	2507	2	2310	2	244	26

that Washburn corrections were much smaller than experimental errors and hence their appreciation was deemed unnecessary. A general illustration of the calculation of the enthalpies of formation is given below:

$$MC_aH_bS_cO_d(C)+\left(\frac{4a+b-2d+6c+4x}{4}\right)O_2(g)+\left(\frac{232-b}{2}\right)H_2O(1)$$
$$\to MO_x(C)+aCO_2(g)+cH_2SO_4,115\,H_2O(1), \qquad (2)$$

$$cH_2(g)+\frac{c}{2}O_2(g)\to cH_2O(1). \qquad (3)$$

Combining equations 1, 2 and 3, one can arrive at

$$MC_aH_bS_cO_d(C)+eO_2(g)\to MO_x(C)+aCO_2(g)+H_2O(1)\frac{b}{2}(1)+cS(C) \qquad (4)$$

where e stands for the summation of the appropriate a, b, c, d and x values.

From this, $\Delta H_{comb.}$ can be calculated.

$$\Delta H_{comb.}=\Delta H_f^0 MO_x(c)+a\Delta H_f^0 CO_2(g)+\frac{b}{2}\Delta H_f^0 H_2O(1)$$
$$-\Delta H_f^0 MC_aH_bS_cO_d(c). \qquad (5)$$

Therefore,

$$\Delta H_f^0 MC_aH_bS_cO_d(S)=\Delta H_f^0 MO_x(c)+a\Delta H_f^0 CO_2(g)$$
$$+\frac{b}{2}\Delta H_f^0 H_2O(1)-\Delta H_{comb.} \qquad (6)$$

The values so obtained are listed in column 3 of Table I. Standard deviations for the values reported in this work were computed from the standard deviations of the terms used in thermochemical calculations, using the formula[15]

$$(n\sigma F)^2 = (a\sigma x)^2 + (b\sigma y)^2 + (c\sigma z)^2$$

where F is a function of the type $nF = ax + by + cz$ with x, y and z, independent of one another and σF, σX, σY and σZ, being the standard deviations in F, X, Y and Z. The standard deviations of the known quantities were taken as zero as is the normal practice. The conventional practice of accepting twice the standard deviation of the mean as the experimental uncertainty has normally been followed. But when more than one quantity is involved as in the present case, the standard deviation is calculated as per the above-cited equation.

The empirical thermochemical cycle, proposed by Jones[1] and later extended by Athavale *et al*[3], was applied in this case with some modifications to calculate the enthalpies of chelation of the complexes in the gaseous phase. A typical cycle for magnesium is given in Fig. 1. The enthalpies of chelation in the condensed phase could be calculated from the above values, again using a modified form of thermochemical cycle which is shown in Fig. 2. In this case, it has been assumed that the enthalpy of sublimation of the complex equals that of the ligand and the vaporisation enthalpy of the appropriate number of water molecules. The hydration energies are small compared to the other enthalpy values encountered in the present work. And hence, the difference between the binding energies of the dihydrates and tetrahydrates has been taken as negligible (Table I). The thermochemical values, *e.g.*, $\Delta H_f^0 H_2O(1)$, etc., used for these calculations have been taken from the literature. The $\langle D\rangle$(O–H) and $\langle D\rangle$(H–H) values used were 460.0 and 431.0 kJ mole^{-1}, respectively[16]. Even though these values may vary from compound to compound[6,17–19] the values used by us are the most average value for many of the organic compounds.

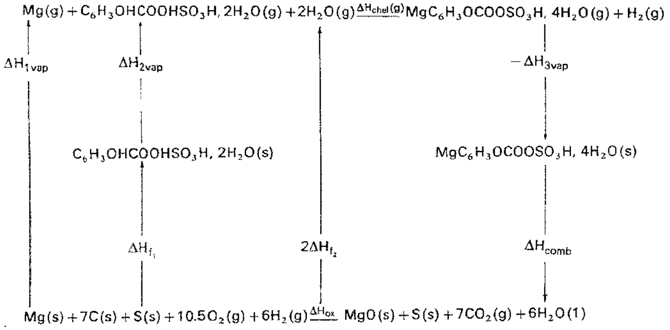


FIG. 1. Empirical thermochemical cycle for enthalpies of chelation in gaseous phase for magnesium sulphosalicylate, tetrahydrate.

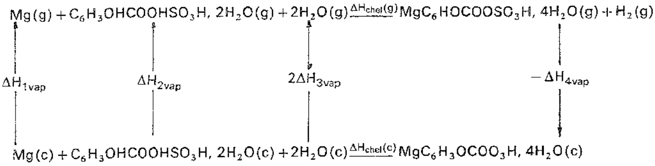
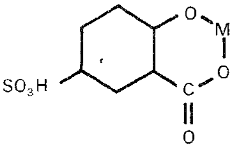


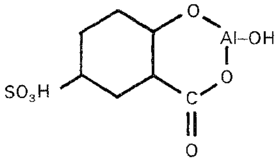
FIG. 2. Empirical Born-Haber cycle for enthalpies of chelation in condensed phase for magnesium sulphosalicylate, tetrahydrate.

For the calculation of the bond dissociation enthalpies the structures of the sulphosalicylates were taken as



where M = Mg, Ca or Zn.

In the case of the aluminium complex the structure was found to be as follows.



This is in accordance with the structure of aluminosalicylic acid. Considering the two M–O bonds in each case as equivalent, the mean molar-bond dissociation enthalpy in the compound can be defined as half the molar enthalpy of the disruption reaction. In other words, the heats of chelation in the gaseous phase of a particular complex can be taken as the summation of various bond dissociation and formation enthalpies involved in the gaseous metal complex. The enthalpies of vaporisation of the ligand and also those of the complexes were assumed safely as $100 \pm 15\,\mathrm{kJ\,mole^{-1}}$. This is purely an estimate of reasonable nature. $\Delta H_{(sub)}$ of salicylic acid has been reported in literature[20-22] as $95.7 \pm 0.8\,\mathrm{kJ\,mole^{-1}}$ and $94.8 \pm 0.4\,\mathrm{kJ\,mole^{-1}}$. Based on this we have assumed the above cited value for $\Delta H_{(sub)}$ of sulphosalicylic acid. This conclusion is based on the study of various similar ligands and complexes undertaken in our laboratory and the uncertainty is not expected to be above $\pm 15\,\mathrm{kJ\,mole^{-1}}$. Thus the values of the mean-bond dissociation enthalpies of the bonds Al–O, Mg–O, Ca–O and Zn–O in the respective complexes can be calculated. These values together with the respective values reported for compounds not containing sulphonic acid group are given in Table II.

Homolytic and heterolytic bonds are related to each other in the following way[23].

$$n\Delta \mathrm{H}(\mathrm{M{:}L})_{\mathrm{homo}} = n\Delta \mathrm{H}(\mathrm{M{:}L})_{\mathrm{hetero}} + \sum_{i=1}^{n} I_i + n\left(\frac{5}{2}\mathrm{RT}\right) - nE_L$$

where $\Sigma_{i=1}^{n} I_i$ is the ionisation potential summation of the metal atom and E_I is the electron affinity of the ligand.

The ionisation potential summation values for zinc, calcium, magnesium and aluminium are readily available in the literature. The electron affinity parameters, E_I, of the ligand sulphosalicylic acid could not be obtained. However, as the bonding takes place through oxygen, this value could be taken as that of oxygen, *viz.*, 142 kJ mole^{-1}. Any variation on this value would be a constant factor affecting equally all the calculations.

Table III summarises the homolytic and the heterolytic contribution to the bond enthalpies between the respective metals and oxygen in the sulphosalicylates.

Table II
Mean dissociation enthalpies (kJ mole^{-1} at 298°K)

Compound	Bond	Value obtained	Standard deviation	Value reported
Alumino sulphosalicylic acid, tetrahydrate	Al–O	277	10	279[25], 266[4]
Calcium sulphosalicylate, dihydrate	Ca–O	376	14	400[26]
Magnesium sulphosalicylate, tetrahydrate	Mg–O	335	12	292[1]
Zinc sulphosalicylate tetrahydrate	Zn–O	232	8	221[27]

Table II
Homolytic and heterolytic values (in kJ mole^{-1} at 298°K)

Metal	$\Sigma_{i=1}^{n} I^i$	nE	$\Delta \mathrm{H}(\mathrm{M{:}L})_{\mathrm{homo}}$	$\Delta \mathrm{H}(\mathrm{M{:}L})_{\mathrm{hetero}}$
Aluminium	5138	427	277	5562
Calcium	1735	285	376	2214
Magnesium	2188	285	335	2587
Zinc	2639	285	214	2831

The results in Table II indicate that the introduction of a highly polar group, *viz.*, sulphonyl, does not make any notable impact on the mean-molar dissociation enthalpies for the M–O bond where M = Ca, Zn, Mg or Al. The constancy of the bond-dissociation enthalpies indicates that for a certain metal, this value is not affected by the structure of the ligand.

It can be expected that the metal-oxygen bonds in the inner complexes are more or less similar to the corresponding bonds of the crystalline metal oxides[7] on considering the process

$$M_xO_y(C) \xrightarrow{\Delta H_{diss}} xM,(g) + yO(g)$$

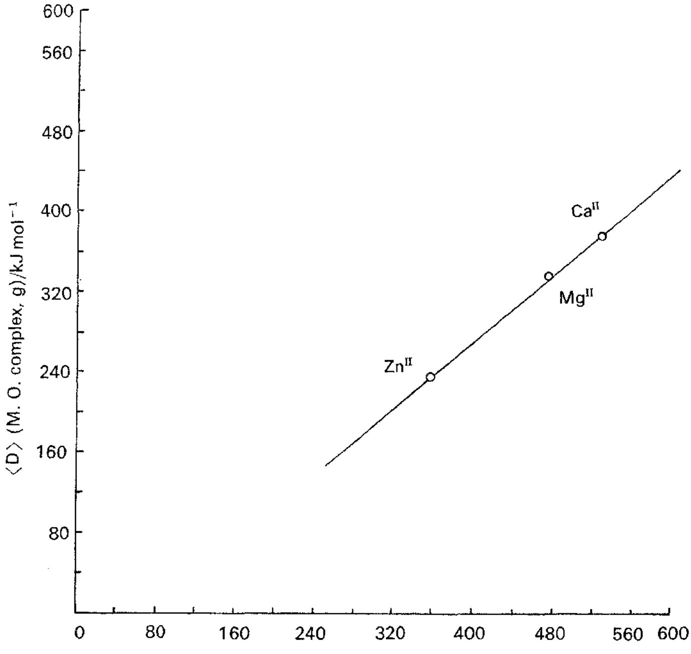


FIG. 3. Variation of $\langle D \rangle$ (M.O. complex, c) with $\langle D \rangle$ (M.O. oxide, c).

and defining a parameter

$$\langle D\rangle(\text{M–O, oxide, C}) = \frac{\Delta H_{\text{diss}}}{\text{coordination number of metal}}.$$

A plot of $\langle D\rangle$(M–O, complex, *g*) *versus* D (M–O, oxide, C) should be a straight line. Figure 3 shows the correlation between these quantities. It could be assumed from the linearity that the metal is surrounded by the oxygen atoms of two ligands and so, in other words, gets totally oxidised. This is similar to the degree of oxidation obtained to the corresponding metal oxide. Because of the valency difference between aluminium and the other metal (aluminium being trivalent), the relation was not applied to aluminium.

In a very recent work[24], Airoldi and Santos have determined the mean-bond dissociation enthalpy of the Ca–O bond in hexa bis (urea) calcium bromide as $295 \pm 9\,\text{kJ mole}^{-1}$. However, the calculation of this quantity for ionic complexes requires a knowledge of the bond length which is not available at present. Consequently, thermochemical quantities involving this class of complexes are very limited. In view of the ionic nature of the above compound, the difference between their value and our value is as anticipated.

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