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Empirical correlations involving calorimetric, thermogravimetric and infrared data for zinc halides adducts

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Abstract

The use of the non-isothermal Coats–Redfern method to obtain the activation energy values for the processes $ZnX_2 \cdot 2hmpa(c) \rightarrow ZnX_2(c) + 2hmpa(g)$ (X = Cl, Br, I and hmpa = hexamethylphosphoramide), by using thermogravimetric data, gave the values 44; 94 and 215 kJ mol⁻¹ for the given sequence of halides. These values correlated to the standard molar enthalpy of formation in the condensed phase for the same sequence of adducts: -1596, -1532 and -1408 kJ mol⁻¹, respectively, providing the equation: $\Delta_f H_m^\circ = 1.086 \times E_a - 1639.738$, which shows a linear correlation between the thermodynamic and kinetic parameters for such solid adducts. The IR spectroscopy data for a series of adducts of zinc halides with amides enabled the acquisition of an equation to estimate the mean metal–ligand bond enthalpy $\langle D \rangle (M-L)$ values: the spectroscopic data were adjusted to the expression $\langle D \rangle (M-L) = \alpha + \beta + \Delta v$, where α and β are related to Lewis acidity and basicity coordination features, respectively, and Δv is the difference between C=O or P=O stretching vibrations of the coordinated and uncoordinated ligands. This equation was applied for 15 adducts, showing a deviation less than 10% from the thermochemical values. (© 2002 Published by Elsevier Science Ltd.)

Keywords: Zinc adducts; Emprirical correlations; Calorimetry; Infrared spectroscopy

1. Introduction

Thermochemical investigations allowed the determination of series of parameters connecting the condensed and gaseous phases of adducts, and from them some chemical and physical properties for such a class of compounds can be deduced [1]. In such calorimetric studies, the first step involved is to obtain the standard molar enthalpy of an acid–base reaction in the condensed phase. This precursor value is used in an appropriated thermochemical cycle with other auxiliary data, relating to the acid and base components, to determine the mean metal–ligand bond enthalpy [1,2], and the acquisition of such an enthalpic value, $\langle D \rangle (M-$ L), continues to be the main objective in coordination chemistry calorimetric studies.

Based on an extensive study involving adducts, the results were systematized in the hypothesis [1] that

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 $\langle D \rangle (M-L) = -\Delta_g H_m^{\circ}/n$. In this expression, $\Delta_g H_m^{\circ}$ is the acid-base interaction enthalpy in the gaseous phase, associated to a given number n of ligands. However, the difficulty in using this equation is related to the fact that the $\Delta_{g}H_{m}^{\circ}$ value is rarely available, and its determination involves not only special experimental conditions but also depends on the intrinsic stability of the compound on heating. This last feature manifests as a consequence of a weak bond formation between the acidic and basic species. In such a direction, the great majority of adducts decompose before subliming.° value is rarely available, and its determination involves not only special experimental conditions but also depends on the intrinsic stability of the compound on heating. This last feature manifests as a consequence of a weak bond formation between the acidic and basic species. In such a direction, the great majority of adducts decompose before subliming.

Taking into account a number of sublimable adducts, being the most representative the complexes formed with the ligand thiourea [3], it was established that the

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enthalpy of sublimation of 1 mol of adduct is equal to the enthalpy of sublimation of one mol of the ligand [1]. So it was assumed that the intermolecular forces in the adduct and ligand should be very similar since the crystalline structure of the ligand complex remains virtually unchanged in the gaseous phase. Such hypothesis was confirmed by experimental results, since the obtained enthalpy values exhibited a variation [4] within ± 10 kJ mol⁻¹.

The purpose of this paper is to report the nonisothermal kinetic thermogravimetric study for the adducts $ZnX_2 \cdot 2hmpa(c)$ (X = Cl, Br, I and hmpa = hexamethylphosphoramide), as well as showing that some thermochemical parameters normally measured or calculated by using reaction-solution calorimetry data, can also be estimated from thermogravimetric or spectroscopic (IR) data. So, a series of empirical correlations involving calorimetric, t.g. and IR data are established.

2. Experimental

The adducts of the general formula $ZnX_2 \cdot 2hmpa$ (X = Br and I; hmpa = hexamethylphosphoramide) were prepared as previously described [5]. A slight excess of the ligand in relation to the desired stoichiometry was added to the metal halide solution in light petroleum ether. The resulting solution was stirred and warmed to 60 °C to allow the complete dissolution of the salt. Upon cooling, the adduct started to settle and the solid was filtered off, washed with ether and dried in vacuum.

The adduct $ZnCl_2 \cdot 2hmpa$ was obtained by the direct dissolution of a stoichiometric amount of the metal halide in pure ligand. The product was washed with double distilled water and dried under vacuum at 30 °C for 10 h.

The elemental analysis was performed on a Perkin– Elmer CHN analyzer. The IR spectra were obtained on a Bomem spectrophotometer in KBr discs. The thermogravimetric curves were obtained on a DuPont apparatus, model 1090B, under argon atmosphere, with a heating rate of 5 °C min⁻¹. The scanning differential calorimetric (DSC) curves were obtained under the same conditions, by using DuPont 2000 equipment.

The kinetic parameters for the thermal degradation of the three adducts were calculated through the Coats– Redfern method [6], employing the data collected in the non-isothermal thermogravimetric curves.

3. Results and discussion

3.1. Solution calorimetry, t.g. and d.s.c data

The obtained IR results are in agreement with a coordination involving the P=O group of the hmpa molecule [5]. The thermogravimetric curves for the three synthesized adducts are shown in Fig. 1. All calculated kinetic parameters obtained through the Coats-Redfern method [6] are listed in Table 1.

The profile of the thermogravimetric curves of these adducts clearly showed that the thermal stability of the



Fig. 1. Thermogravimetric curves for the adducts $ZnX_2 \cdot 2hmpa$: X = chloride (a), bromide (b) and iodide (c).

Table 1 Kinetic parameters calculated through Coats–Redfern method for the non-isothermal degradation of the adducts ZnX₂·2hmpa

$ZnX_2 \cdot 2hmpa$	$E_{\rm a}$ (kJ mol ⁻¹)	A	n
Cl	44	3.1×10^{3}	1
Br	94	6.6×10^{6}	1
I	215	4.4×10^{23}	1

 $E_{\rm a}$ is the activation energy, A is the frequency or pre-exponential factor and n is the order of reaction.

compounds decreased in the order: Cl < Br < I. This is the same sequence found for the activation energy (E_a) values for the corresponding thermal degradation processes: $ZnX_2 \cdot 2hmpa(c) \rightarrow ZnX_2(c) + 2hmpa(g)$.

Based on the collected data, the ratio between t_i , the Kelvin temperature of the beginning of the thermal degradation, and the corresponding E_a values listed in Table 1, gives: $387/44 = 2.63 \ 395/94 = 4.20$ and 440/215 = 8.80. These data can be summarized by the empirical equation: t_i (K)/ E_a (kJ mol⁻¹) $\cong 2^b$, which exponential value ranges from 1 to 3. A plot of E_a values as function of t_i is shown in Fig. 2. As can be observed, a straight line is obtained with a coefficient of correlation of 0.99, providing the empirical equation:

$$E_a = 3.043 \times t_i - 1122.130 \tag{1}$$

The standard molar enthalpy of formation of the considered adducts in the condensed phase presented the following values: -1596, -1532 and -1408 kJ mol⁻¹ for chloride, bromide and iodide [5], respectively. By plotting this sequence of values as function of the E_a values, again a straight line was obtained as shown in Fig. 3. Then, a new empirical equation was established as:

$$\Delta_{\rm f} H_{\rm m}^{\circ} = 1.086 \times E_{\rm a} - 1639.738 \tag{2}$$



Fig. 2. Activation energy values (E_a kJ mol⁻¹) as a function of the Kelvin temperature for the beginning of the thermal degradation (t_i K), for the ZnX₂·2hmpa adducts.



Fig. 3. Standard molar enthalpy of formation $(\Delta_f H_m^{\circ} \text{ kJ mol}^{-1})$ as function of the activation energy for the thermal degradation process $(E_a \text{ kJ mol}^{-1})$, for ZnX₂·2hmpa adducts.

This obtained equation opens the possibility of estimates for an enthalpic value, which is normally obtained from calorimetric measurements, by using a simple kinetic parameter derived from thermogravimetric data.

The order of reaction 'n' obtained for the thermal degradation processes gives a unity value for these three adducts, as listed in Table 1. Such a fact suggests a similar behavior for the adducts on heating, which implies a certain degree of isomorphism [7]. The temperatures of fusion, $t_{\rm fus}$, determinated by DSC analysis gave the values 108, 125 and 166 °C for the chloride, bromide and iodide adducts, respectively. The increase in melting temperature values suggests an enhancement of the intermolecular interactions of the adducts from chloride to iodide. This sequence is in agreement with t_i as well as E_a values. The relationship $t_i/t_{\rm fus}$ is almost constant and near to unity for the three adducts; respectively.

The lattice enthalpy $(\Delta_M H_m^\circ)$ for the adducts, associated with the process: $ZnX_2 \cdot 2hmpa(c) \rightarrow ZnX_2(g) +$ 2hmpa(g), was calculated to give [5] 375; 380 and 365 kJ mol⁻¹, for Cl, Br and I, respectively. These values enabled the acquisition of an interesting empirical equation related to melting temperature, t_{fus} . As observed for dimethylethyleneurea adducts [8], the lattice enthalpy values are adjusted to the empirical equation [9]:

$$\Delta_{\rm M} H^{\circ}_{\rm m} = 0.11 \times M \times \Delta^{\rm l}_{\rm cr} H^{\circ}_{\rm m} (t_{\rm fus}) \tag{3}$$

where *M* is the molar mass of the ligand and $\Delta_{cr}^{l} H_{m}^{\circ}(t_{fus})$ is the enthalpy of melting of these adducts, at the melting temperature, as determined by DSC data, whose values are 18.90, 19.52 and 16.46 kJ mol⁻¹, for chloride, bromide and iodide adducts, respectively.

3.2. Themochemistry and IR spectroscopy

From the point of view of coordination chemistry, the nature of the donor atom on the ligand molecule as well as the number of ligands involved in bond formation are associated to important features related with the mean metal-ligand bond enthalpy, $\langle D \rangle (M-L)$ [4,10,11].

To establish an equation relating thermochemical and IR data, only adducts of zinc halides with two ligands, which are generally tetrahedral, were chosen. The selected adducts of zinc halides are those with urea (u) [12], methylurea (mu) [13], dimethylurea (dmu) [14], dimethylformamide (dmf) [15] tetramethylurea (tmu) [16], dimethylacetamide (dma) [17], dimethylethyleneurea (dmeu) [8], ε -caprolactam (cl) [18], γ -butyrolactam (bul) [19] and hexamethylphosphoramide (hmpa) [5]. In these adducts, all ligands coordinate through oxygen, and so C=O or P=O stretching frequencies of such ligands decrease upon coordination [1-5,7-19]. For this series of adducts, it is observed that the mean zinc-oxygen bond enthalpy $\langle D \rangle$ (Zn-O) is correlated to the variation (decrease) in the stretching frequency Δv , of the C=O or P=O groups (free ligand-coordinated ligand). Based on this fact, the following empirical equation is proposed:

$$\langle \mathbf{D} \rangle (\mathbf{Z}\mathbf{n} - \mathbf{O}) = \alpha + \beta + \Delta v$$
 (4)

where α and β represent the acidic and basic contributions associated with metal halide and ligand, respectively.

The decrease in α values from chloride to iodide, as shown in Table 2, is followed by the tendency in increasing the anionic radii, which also imply an enhancement of their polarizability. On the other hand, β values comprise the donor ability as well as the steric effect of the molecule of the ligand. For example, by considering a sequence of similar ligands, an increase in β values occurred from urea to methyurea, giving 73 and 92, respectively. However, these values decrease progressively from methyl- to tetramethylurea, which has a value of 27. This behavior

Table 2

Values of α for zinc halides, ZnX₂, and β for a series of oxygen donor atom ligands

ZnX ₂	α	Ligand	β
Cl	25	dmf	82
Br	19	u	73
L	15	mu	92
		dmu	88
		tmu	27
		dma	60
		dmeu	84
		cl	96
		bul	77
		hmpa	90

can be explained taking into account the positive inductive effect of the methyl groups (increased basicity of the donor atom) as well as their effect from the point of view of steric hindrance (larger metal–ligand bond lengths). So, the β values reflects the basicity as well as volume of the ligand molecule.

The α and β values shown in Table 2 were established as follows: the Δv experimental values for adducts with zinc halides and dmf [15] were chosen and a value of 25 was attributed for α , associated with ZnCl₂. From this value, α values for ZnBr₂ and ZnI₂ were also calculated as well as β for the same ligand. Afterwards, using the experimental data from adducts of ZnCl₂ and the other ligands, a complete series of β values were established.

The second step is dedicated to the application of the proposed equation by using the parameters shown in Table 2 for the adducts $ZnX_2 \cdot 2L$ (X = Br, I and L = u, mu, dmu, tmu, dma, dmeu, cl, bul, hmpa). The collected results obtained are listed in Table 3, where the thermochemical (calorimetric) and IR $\langle D \rangle$ (Zn–O) values are compared.

The results derived from IR data shows a relatively good agreement with the thermochemical data. To evaluate how good the IR results are, one needs to bear in mind that: (a) thermochemical data for $\langle D \rangle (M - O)$ are obtained from $\Delta_g H_m^{\circ}$ values. In that case, the adduct must be found in the gaseous phase, whereas Δv values are calculated from infrared spectra obtained for solid adducts; (b) α and β values for metal halides and ligands were obtained from $\langle D \rangle (M-O)$ thermochemical data, which were calculated considering that the enthalpy of sublimation for adducts is equal to the enthalpy of sublimation for the respective ligands. Such a hypothesis is based on a series of sublimable adducts, and could not be true for all adducts; (c) Δv

Table 3

The mean zinc–ligand bond enthalpy $\langle D \rangle (Zn-O)$ (kJ mol⁻¹) values, based on thermochemical (ther.) and infrared (IR) data for $ZnX_2 \cdot 2L$ adducts

Adduct	Thermochemical	Infrared	$\Delta^{0\!\!/_0}$ a
$ZnBr_2 \cdot 2u$	139	130	-6.5
$ZnI_2 \cdot 2u$	145	138	4.8
$ZnBr_2 \cdot 2mu$	123	141	14.6
$ZnBr_2 \cdot 2dmu$	136	145	6.6
$ZnBr_2 \cdot 2tmu$	135	141	4.4
$ZnI_2 \cdot 2tmu$	149	140	-6.0
$ZnBr_2 \cdot 2dma$	136	129	-5.1
$ZnI_2 \cdot 2dma$	131	116	-11.5
$ZnBr_2 \cdot 2cl$	128	145	13.3
$ZnI_2 \cdot 2cl$	121	144	19.0
ZnBr ₂ ·2bul	122	119	-2.5
$ZnI_2 \cdot 2bul$	118	130	10.2
ZnBr ₂ ·2hmpa	162	155	-4.3
$ZnI_2 \cdot 2hmpa$	154	151	-1.0
$ZnBr_2 \cdot 2dmeu$	137	137	0.0

^a Δ [%] = (infrared – thermochemical) × 100.

were assumed to contain only C=O or P=O stretching vibrational modes. In reality, there are other components included in such vibrational modes [20,21] that could not be completely considered and are, of course, different for each ligand molecule. Nevertheless, taking into account all these facts, the results obtained may be considered quite good.

For adducts of zinc halides with dmf [15] the metalligand stretching frequency values, v(M-L) are available in the range from 412 to 420 cm⁻¹. From these values an empirical correlation was also established. Then, the relationship between v(M-L) and $\langle D \rangle (Zn-O)$ values was obtained and the results are presented in Table 4.

The ratio involving $v(M-L)/\langle D \rangle (M-L)$ increases from chloride to iodide, reflecting the increase of the anion radii. Another observation related to these values comes from the fact that the considered ratio is nearly equal to n+1, where n is the number of ligands.

These series of data open the possibility of estimating $\langle D \rangle$ (M–O) values by using IR results, establishing an exciting connection between spectroscopy and calorimetry.

4. Conclusion

The obtained experimental results lead to the establishment of a series of empirical equations relating calorimetric, thermogravimetric and IR data. The very simple observed empirical relations could be explored to achieve a most profound knowledge of the physical and chemical behavior of adducts. These kinds of correlations were not restricted to zinc adducts, since they were also observed for copper and cobalt adducts with cyclic amides [22,23] or amino acids [24].

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Table 4 $\nu(Zn-L)/\langle D \rangle(Zn-L)$ values for $ZnX_2 \cdot ndmf$ adducts

Adduct	$\nu(Zn-L)/\langle D \rangle(Zn-L)$	
$ZnCl_2 \cdot 2dmf$	3.0	
$ZnBr_2 \cdot 2dmf$	3.1	
ZnI ₂ .2dmf	3.3	
ZnCl ₂ ·dmf	2.1	
$ZnBr_2 \cdot dmf$	2.2	
$ZnI_2 \cdot dmf$	2.3	