

ESTIMATING THE VALUE OF THE METAL-LIGAND BOND DISSOCIATION ENTHALPY <D> (M-L) FOR ADDUCTS USING EMPIRICAL EQUATIONS SUPPORTED BY TG DATA

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Recebido em 11/12/97; aceito em 10/11/98

In this work is presented and tested (for 106 adducts, mainly of the zinc group halides) two empirical equations supported in TG data to estimate the value of the metal-ligand bond dissociation enthalpy for adducts: $\langle D \rangle (M-O) = t_i / \gamma$ if $t_i < 420$ K and $\langle D \rangle (M-O) = (t_i / \gamma) - 7,75 \cdot 10^{-2} \cdot t_i$ if $t_i > 420$ K. In this empirical equations, t_i is the thermodynamic temperature of the beginning of the thermal decomposition of the adduct, as determined by thermogravimetry, and γ is a constant factor that is function of the metal halide considered and of the number of ligands, but is not dependant of the ligand itself. To half of the tested adducts the difference between experimental and calculated values was less than 5%. To about 80% of the tested adducts, the difference between the experimental (calorimetric) and the calculated (using the proposed equations) values are less than 15%.

Keywords: metal-ligand bond enthalpy; adducts; empirical equations; thermogravimetry.

INTRODUCTION

In the thermochemical study of adducts, the value of the metal-ligand bond dissociation enthalpy is estimated using the equation: $\langle D \rangle (M-L) = - \Delta_g H_m^\circ / n$, where $\Delta_g H_m^\circ$ is the Lewis acid (metal halide) - Lewis base (ligand) gaseous phase reaction enthalpy, calculated as $\Delta_g H_m^\circ = \Delta_f H_m^\circ + \Delta_{sub} H_m^\circ (MX_m \cdot nL) - n \Delta_{sub} H_m^\circ (L) - \Delta_{sub} H_m^\circ (M X_m)$ where MX_m represents a metal halide, L is the ligand and n is the number of ligands. That is, to calculate $\langle D \rangle (M-L)$ we need the value of $\Delta_f H_m^\circ$ which is determined calorimetrically as described in detail elsewhere^{1,2} the value of $\Delta_{sub} H_m^\circ (M X_m)$ (generally found in the literature) and the values of $\Delta_{sub} H_m^\circ (L)$ (the enthalpy of sublimation or vaporization of the ligand) and $\Delta_{sub} H_m^\circ (MX_m \cdot nL)$. At this point, we have two problems: the value of $\Delta_{sub} H_m^\circ (L)$ generally is not found in the literature for many ligands and so, must be measured, by using vapor pressure data (for liquids), or by the Knudsen technique (for solid samples). If a measurement is not possible, the $\Delta_{sub} H_m^\circ (L)$ value must be estimated (by DSC data or another technique). The value of $\Delta_{sub} H_m^\circ (MX_m \cdot nL)$ could not be determined, since the great part of the adducts, take thermal degradation before sublimation³. To overcome this difficulty, the widely used assumption take the value of $\Delta_{sub} H_m^\circ (MX_m \cdot nL)$ as been equal $\Delta_{sub} H_m^\circ (L)$ ³, but this assumption could not be so correct to some compounds.

Since thermogravimetry is a very quick and easy technique to use, requiring only few mg of material for one analysis, should be really useful some kind of quantitative relation between thermogravimetric data and calorimetric ones.

In previous works^{4,6}, were found some mathematical relations (empirical equations) between the value of t_i , that is, the thermodynamic temperature (SI unit: Kelvin) of the beginning of the thermal decomposition of adducts (as determined by thermogravimetry) and some thermochemical parameters, making possible estimate the values of $\Delta_f H_m^\circ$ ⁴ (formation enthalpy), $\Delta_M H_m^\circ$ ⁵ (lattice enthalpy) and $\Delta_D H_m^\circ$ ⁶ (decomposition enthalpy), for adducts, by using thermogravimetric data.

In this work are presented and tested for 106 adducts two empirical equations to estimate the value of $\langle D \rangle (M-L)$, the mean metal-ligand bond dissociation enthalpy, by using thermogravimetric data.

OBTAINING THE EQUATIONS

As in previous works⁴⁻⁶, the adducts with dimethylformamide (dmf) and the zinc group halides^{7,8} were used as models to obtain the empirical equations, but with no special reasons to do this, only by a question of choice.

Searching for the possible mathematical relations between the thermochemical and the thermogravimetric data for that adducts, two empirical equations were obtained, correlating the mean metal-ligand bond dissociation enthalpy $\langle D \rangle (M-L)$ and t_i , the thermodynamic temperature of the beginning of the thermal decomposition of the adduct, as obtained by thermogravimetry:

$$\langle D \rangle (M-L) = t_i / \gamma \quad (1)$$

if $t_i < 420$ K and

$$\langle D \rangle (M-L) = (t_i / \gamma) - 7,75 \cdot 10^{-2} \cdot t_i \quad (2)$$

if $t_i > 420$ K

The γ values are function of the metal halide and of the number of ligands. The γ values for adducts with 1 and 2 ligands were obtained using the thermogravimetric and calorimetric data for dmf and zinc group halides adducts^{7,8}. The γ values for adducts with 3 ligands were obtained by extrapolation, assuming that, the increase (in percentage) in the value of γ from 2 to 3 ligands, is the same that is observed from 1 to 2 ligands. The values of γ for adducts with fractionary number of ligands, were obtained assuming that, for this adducts, the values of γ are the average values for adducts with integer number of ligands. For example, the values of γ for adducts with 1.5 ligand is considered as been the average value of γ for adducts with 1 and 2 ligands. The values of γ are presented in table 1.

RESULTS AND DISCUSSION

The proposed equations were tested for a total of 106 adducts: adducts with zinc group halides and ϵ -caprolactam (cl)¹, 2-pyrrolidone (butyrolactam-bul)², tioacetamide (ta)⁹, tiobenzamide

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Table 1. γ values for Zn group halides as a function of the number of ligands

| Metal halide | γ (number of ligands) | | | | |
|-------------------|------------------------------|-------|------|-------|------|
| | (1) | (1.5) | (2) | (2.5) | (3) |
| ZnCl ₂ | 2,00 | 2,33 | 2,65 | 3,08 | 3,51 |
| ZnBr ₂ | 2,30 | 2,54 | 2,77 | 3,06 | 3,34 |
| ZnI ₂ | 2,55 | 2,74 | 2,92 | 3,32 | 3,72 |
| CdX ₂ | 2,10 | 2,40 | 2,68 | 3,05 | 3,42 |
| HgX ₂ | 3,25 | 3,68 | 4,10 | 4,67 | 5,23 |

X = Cl, Br or I .

(tb)⁹, methylurea (mu)¹⁰, dimethylurea (dmu)¹⁰, tetramethylurea (tmu)¹⁰, urea (u)^{11,12}, hexamethylfosforamide (hmpa)¹³, triphenylfosfinoxide (tppo)^{13,14}, aniline (an)¹⁵, dimethylacetamide (dma)¹⁶, and dimethylethyleneurea (dmeu)¹⁷; adducts with Sb and Bi triiodides and tetramethyltiourea (tmtu)¹⁸, dimethyltioacetamide (dmta)¹⁹ and dimethyltioformamide (dmtf)¹⁹; adducts with halides of As and pyridine (py)²⁰, β -pycoline (β -mpy) 20 and γ -pycoline (γ -mpy)²⁰.

The results obtained are presented in Table 2.

Table 2. Experimental and calculated values of $\langle D \rangle$ (M-L) for some adducts with Zn and As group halides

| Adduct | t_i / K | $\langle D \rangle$ (M-O)/ kJ mol ⁻¹ | | $\Delta\%$ * |
|----------------------------|-----------|---|------------|--------------|
| | | Experimental | Calculated | |
| ZnCl ₂ .2dmeu | 366 | 139 | 138 | -0,7 % |
| ZnBr ₂ .2dmeu | 377 | 137 | 136 | -0,7 % |
| ZnCl ₂ .3cl | 371 | 134 | 106 | -21,0 % |
| ZnCl ₂ .2cl | 415 | 154 | 157 | 1,9 % |
| ZnBr ₂ .3cl | 356 | 123 | 107 | -13,0 % |
| ZnBr ₂ .2cl | 403 | 128 | 146 | 14,1 % |
| ZnI ₂ .3cl | 368 | 118 | 99 | -16,1 % |
| ZnI ₂ .2cl | 414 | 121 | 142 | 17,4 % |
| ZnCl ₂ .3bul | 353 | 112 | 101 | -9,8 % |
| ZnCl ₂ .2bul | 384 | 132 | 145 | 9,8 % |
| ZnBr ₂ .3bul | 355 | 105 | 106 | 0,9 % |
| ZnBr ₂ .2bul | 391 | 122 | 141 | 15,6 % |
| ZnI ₂ .3bul | 304 | 103 | 82 | -20,4 % |
| ZnI ₂ .2bul | 400 | 118 | 137 | 16,1 % |
| ZnCl ₂ .2u | 412 | 148 | 155 | 4,7 % |
| ZnBr ₂ .2u | 402 | 139 | 145 | 4,3 % |
| ZnI ₂ .2u | 409 | 145 | 140 | -3,4 % |
| ZnCl ₂ .2hmpa | 388 | 113 | 146 | 29,2 % |
| ZnBr ₂ .2hmpa | 398 | 124 | 144 | 16,1 % |
| ZnI ₂ .2hmpa | 418 | 122 | 143 | 17,2 % |
| ZnCl ₂ .2an | 380 | 144 | 143 | -0,7 % |
| ZnBr ₂ .1,5an | 393 | 157 | 157 | 0,0 % |
| ZnBr ₂ .2tppo | 498 | 134 | 141 | 5,2 % |
| ZnI ₂ .2tppo | 508 | 125 | 135 | 8,0 % |
| ZnCl ₂ .2ta | 468 | 147 | 141 | -4,1 % |
| ZnCl ₂ .2tb | 450 | 152 | 135 | 11,2 % |
| ZnCl ₂ .2tmu | 364 | 142 | 137 | -3,5 % |
| ZnCl ₂ .2dmu | 454 | 145 | 136 | 6,2 % |
| ZnCl ₂ .2mu | 441 | 132 | 132 | 0,0 % |
| ZnBr ₂ .2tmu | 390 | 135 | 141 | 4,4 % |
| ZnBr ₂ .2dmu | 467 | 136 | 133 | 2,2 % |
| ZnBr ₂ .2mu | 441 | 123 | 125 | 1,6 % |
| ZnI ₂ .2tmu | 386 | 149 | 132 | -11,4 % |
| ZnCl ₂ .2dma | 386 | 139 | 146 | 5,0 % |
| ZnBr ₂ .2dma | 374 | 136 | 135 | -0,7 % |
| ZnI ₂ .2dma | 388 | 131 | 133 | 1,5 % |
| CdCl ₂ .1,5dmeu | 393 | 155 | 164 | 5,8 % |
| CdBr ₂ .1,5dmeu | 360 | 144 | 150 | 4,2 % |

Table 2 continued

| Adduct | t_i / K | $\langle D \rangle$ (M-O)/ kJ mol ⁻¹ | | $\Delta\%$ * |
|-----------------------------------|-----------|---|------------|--------------|
| | | Experimental | Calculated | |
| CdI ₂ .2dmeu | 343 | 125 | 128 | 2,4 % |
| CdCl ₂ .bul | 418 | 212 | 199 | -6,1 % |
| CdBr ₂ .bul | 405 | 191 | 193 | 1,0 % |
| CdI ₂ .2bul | 369 | 114 | 138 | 21,1 % |
| CdCl ₂ .u | 496 | 203 | 198 | -2,5 % |
| CdBr ₂ .u | 464 | 165 | 185 | 12,1 % |
| CdI ₂ .u | 399 | 168 | 190 | 13,1 % |
| CdBr ₂ .2u | 445 | 132 | 132 | 0,0 % |
| CdI ₂ .2u | 387 | 123 | 144 | 17,1 % |
| CdCl ₂ .2hmpa | 343 | 84 | 128 | 52,4 % |
| CdBr ₂ .2hmpa | 368 | 95 | 137 | 44,2 % |
| CdI ₂ .2hmpa | 373 | 104 | 139 | 33,7 % |
| CdBr ₂ .2tppo | 468 | 117 | 139 | 18,8 % |
| CdI ₂ .2tppo | 458 | 117 | 136 | 16,2 % |
| CdCl ₂ .2an | 380 | 141 | 142 | 0,7 % |
| CdI ₂ .2an | 393 | 127 | 147 | 15,7 % |
| CdCl ₂ .cl | 453 | 208 | 216 | 3,8 % |
| CdBr ₂ .2cl | 377 | 136 | 141 | 3,7 % |
| CdBr ₂ .cl | 433 | 165 | 172 | 4,2 % |
| CdI ₂ .2cl | 398 | 123 | 149 | 21,1 % |
| CdCl ₂ .tmu | 428 | 226 | 171 | -24,3 % |
| CdCl ₂ .dmu | 367 | 210 | 175 | -16,7 % |
| CdCl ₂ .mu | 493 | 204 | 197 | -3,4 % |
| CdBr ₂ .tmu | 349 | 184 | 166 | -9,8 % |
| CdBr ₂ .dmu | 453 | 163 | 181 | 11,0 % |
| CdBr ₂ .mu | 472 | 161 | 188 | 16,8 % |
| CdBr ₂ .3dmu | 428 | 113 | 92 | -18,6 % |
| CdI ₂ .2tmu | 355 | 126 | 133 | 5,6 % |
| CdCl ₂ .dma | 354 | 210 | 169 | -19,5 % |
| CdBr ₂ .dma | 418 | 188 | 199 | 5,9 % |
| CdCl ₂ .tb | 493 | 200 | 197 | -1,5 % |
| CdCl ₂ .2ta | 410 | 155 | 153 | -1,3 % |
| CdI ₂ .2dma | 338 | 123 | 126 | 2,4 % |
| HgCl ₂ .bul | 355 | 111 | 109 | -1,8 % |
| HgBr ₂ .bul | 350 | 109 | 108 | -0,9 % |
| HgCl ₂ .u | 440 | 93 | 101 | 8,6 % |
| HgBr ₂ .u | 432 | 83 | 100 | 20,5 % |
| HgCl ₂ .2hmpa | 328 | 89 | 80 | -10,1 % |
| HgBr ₂ .2hmpa | 348 | 89 | 85 | -4,5 % |
| HgI ₂ .2hmpa | 333 | 83 | 81 | -2,4 % |
| HgBr ₂ .2tppo | 408 | 83 | 100 | 20,5 % |
| HgCl ₂ .1,5dmeu | 344 | 92 | 93 | 1,1 % |
| HgCl ₂ .cl | 411 | 97 | 127 | 31,0 % |
| HgBr ₂ .2cl | 367 | 100 | 90 | -10,0 % |
| HgBr ₂ .cl | 407 | 102 | 125 | 22,5 % |
| HgCl ₂ .tmu | 369 | 119 | 114 | -4,2 % |
| HgCl ₂ .dmu | 426 | 100 | 99 | -1,0 % |
| HgCl ₂ .2dmu | 413 | 92 | 101 | 9,8 % |
| HgCl ₂ .mu | 416 | 97 | 128 | 32,0 % |
| HgBr ₂ .tmu | 365 | 113 | 112 | -0,9 % |
| HgBr ₂ .dmu | 426 | 99 | 99 | 0,0 % |
| HgBr ₂ .mu | 429 | 97 | 99 | 2,1 % |
| HgCl ₂ .dma | 333 | 106 | 103 | -2,8 % |
| HgBr ₂ .dma | 333 | 106 | 103 | -2,8 % |
| AlCl ₃ .py | 311 | 154 | 156 | 1,3 % |
| AlCl ₃ . β mpy | 298 | 164 | 149 | -9,1 % |
| AlCl ₃ . γ mpy | 409 | 164 | 205 | 25,0 % |
| AsBr ₃ .3 β mpy | 298 | 124 | 89 | -28,2 % |
| AsBr ₃ .2 γ mpy | 298 | 129 | 108 | -16,3 % |
| AsI ₃ .2py | 439 | 121 | 116 | -4,1 % |
| AsI ₃ . β mpy | 429 | 155 | 135 | -13,0 % |
| AsI ₃ . γ mpy | 448 | 168 | 141 | -16,1 % |
| SbI ₃ .tmtu | 428 | 122 | 135 | 10,7 % |

Table 2 continued

| Adduct | t _i / K | <D> (M-O) / kJ mol ⁻¹ | | Δ% * |
|------------------------|--------------------|----------------------------------|------------|--------|
| | | Experimental | Calculated | |
| SbI ₃ .dmta | 373 | 112 | 146 | 30,4 % |
| SbI ₃ .dmtf | 373 | 117 | 146 | 24,8 % |
| BiI ₃ .tmtu | 476 | 147 | 150 | 2,0 % |
| BiI ₃ .dmta | 373 | 144 | 146 | 1,4 % |
| BiI ₃ .dmtf | 373 | 150 | 146 | -2,7 % |

* Δ = [(calculated-experimental) / experimental] x 100

To calculate the values of <D> (M-L) for As group halide adducts, the values of γ used were that for zinc group halides.

The fact that there are different values of γ to the different zinc halides whereas the same value of γ is valid for all the halides of cadmium and mercury, suggests that the metal-ligand bond enthalpy in zinc halides adducts are much more sensitive to structural variations (because of variations in the halide radius) than in Cd and Hg adducts. Furthermore, the halide hardness presents the order Cl > Br > I, and, as reported elsewhere¹⁷, the metal cation Zn²⁺ is more sensitive than Cd²⁺ and Hg²⁺ to variations in the hardness of the donor atom in the ligand molecule, which is an example, in adduct chemistry, of the general thermochemical feature observed for hard and soft acid-bases interactions²¹.

Certainly, in the proposed equations, the correct value of t_i is very important. The values of t_i presented in table 2, are that provided by the respective authors^{1,2, 9-20}.

It is necessary pay attention in two important facts : all the ligands presented are monodentate and although the equations were obtained using a ligand that coordinate through oxygen (dmf), its were used too for adducts that coordinate through sulfur and nitrogen.

The results could be summarized as follows : for half of the tested adducts, the difference between the experimental (calorimetric) and the calculated values (using the proposed equations) are less than 5%, which is a very good result. For about 80 % of the tested adducts the difference between experimental and calculated values was less than 15% which could be considered as a good agreement for this kind of procedure.

The generally bad results obtained for adducts with hmpa and tppo (for many adducts the calculated values are greater than the experimental ones) could be, at first, understood as consequence of the esterical hindrance, since that ligands are the bigger ones among the adducts studied, that is, the metal-ligand bond lengths used (implicit) in the calculated values are shorter than the real bond lengths.

The term (-7,75.10⁻²).t_i in equation (2), could be understood

as a correction factor to take in account the contribution of the vibrational heat capacity of the metal-ligand bond.

Since the experimental values of <D> (M-L) are estimations with an error of ± 10 or 15 kJ mol⁻¹, and the t_i values presents an error of ± 5 or 10 K depending on the experimental apparatus used and the calibration procedures, the fact that, to about 40 compounds, the difference between calculated and experimental (calorimetric) values exceeds 10% is not a bad result.

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