

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

Robson Fernandes de Farias*

Departamento de Química - Universidade Federal de Roraima - 69310-270 - Boa Vista - Roraima - Brasil

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 / γ 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) = $-\Delta_g H_m^0 / n$, where $\Delta_g H_m^0$ is the Lewis acid (metal halide) - Lewis base (ligand) gaseous phase reaction enthalpy, calculated as $\Delta_g H_m^0 = \Delta_f H_m^0 + \Delta_{\text{sub}} H_m^0 (MX_m \cdot nL) - n \Delta_{\text{sub}} H_m^0 (L) - \Delta_{\text{sub}} H_m^0 (MX_m)$ 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 $\Delta_f H_m^0$ which is determined calorimetrically as described in detail elsewhere^{1,2} the value of $\Delta_{\text{sub}} H_m^0 (MX_m)$ (generally found in the literature) and the values of $\Delta_{\text{sub}} H_m^0 (L)$ (the enthalpy of sublimation or vaporization of the ligand) and $\Delta_{\text{sub}} H_m^0 (MX_m \cdot nL)$. At this point, we have two problems: the value of $\Delta_{\text{sub}} H_m^0 (L)$ 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 $\Delta_{\text{sub}} H_m^0 (L)$ value must be estimated (by DSC data or another technique). The value of $\Delta_{\text{sub}} H_m^0 (MX_m \cdot nL)$ 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 $\Delta_{\text{sub}} H_m^0 (MX_m \cdot nL)$ as been equal $\Delta_{\text{sub}} H_m^0 (L)$ 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 $\Delta_f H_m^0$ ⁴ (formation enthalpy), $\Delta_M H_m^0$ ⁵ (lattice enthalpy) and $\Delta_D H_m^0$ 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:

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

if $t_i < 420$ K and

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

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, tiacetamide (ta)⁹, tiobenzamide

* present address: Instituto de Química - Universidade Estadual de Campinas - Unicamp - CP 6154 - 13083 970 - Campinas - SP - Brasil
e-mail: rffarias@iqm.unicamp.br

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		$\Delta\%$ *
		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 %

* $\Delta = [(\text{calculated} - \text{experimental}) / \text{experimental}] \times 100$

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 $\text{Cl} > \text{Br} > \text{I}$, and, as reported elsewhere¹⁷, the metal cation Zn^{2+} is more sensitive than Cd^{2+} and Hg^{2+} 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}.

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 $(-7,75 \cdot 10^{-2}) \cdot t_i$ 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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