Standard Enthalpies of Formation of Diamine(dicarboxylato)platinum(II) Complexes and of Bis(pentane-2,4-dionato)platinum(II): the Mean Pt–O Bond Dissociation Enthalpies

Ghassan Al-Takhin, Geoffrey Pilcher,* and James Bickerton
Chemistry Department, University of Manchester, Manchester M13 9PL
Ahmed A. Zaki
Chemistry Department, U.M.I.S.T., Manchester M60 1QD

The following standard enthalpies of formation (kJ mol^{-1}) of the crystalline solids were determined at 298.15 K using solution reaction calorimetry: $\Delta H_f^\ominus\{[Pt\{(O_2C)_2CH_2\}(NH_2CH_2CH_2NH_2)]\} = -974 \pm 7$; $\Delta H_f^\ominus\{[Pt\{(O_2C)_2CHMe\}(NH_2Et)_2]\} = -1\,087 \pm 10$; $\Delta H_f^\ominus\{[Pt\{(O_2C)_2CHEt\}(NH_3)_2]\} = -1\,080 \pm 3$; $\Delta H_f^\ominus\{[Pt\{(O_2C)_2CHEt\}(NH_2Et)_2]\} = -1\,083 \pm 10$; $\Delta H_f^\ominus\{[Pt\{(O_2C)_2CH(OH)\}(NH_3)_2]\} = -1\,193 \pm 3$; $\Delta H_f^\ominus\{[Pt(cbda\text{-}1,1)(NH_3)_2]\} = -959 \pm 3$, ($H_2$cbda-1,1 = cyclobutane-1,1-dicarboxylic acid); $\Delta H_f^\ominus\{[Pt(cbda\text{-}1,1)(NH_2Me)_2]\} = -910 \pm 8$; $\Delta H_f^\ominus\{[Pt(cbda\text{-}1,1)(NH_2Et)_2]\} = -983 \pm 10$; $\Delta H_f^\ominus\{[Pt(cbda\text{-}1,1)(NH_2Pr^i)_2]\} = -1\,095 \pm 6$; $\Delta H_f^\ominus\{[Pt(cbda\text{-}1,2)(NH_2Me)_2]\} = -852 \pm 8$ (H_2cbda-1,2 = cyclobutane-1,2-dicarboxylic acid); $\Delta H_f^\ominus\{[Pt(pd)_2]\} = -687 \pm 5$ (Hpd = pentane-2,4-dione). With estimated enthalpies of sublimation, it was deduced that the sum of the mean bond dissociation enthalpies, $\bar{D}(Pt-N) + \bar{D}(Pt-O) \approx 490$ kJ mol^{-1}. By substituting $\bar{D}(Pt-N)$ from the corresponding $[PtCl_2(NH_2R)_2]$ complexes, $\bar{D}(Pt-O)$ for the diamine(dicarboxylato)platinum complexes ≈ 380 kJ mol^{-1} compared to $\bar{D}(Pt-O) \approx 183$ kJ mol^{-1} in $[Pt(pd)_2]$.

The thermochemistry of platinum compounds has not been systematically studied and no information on platinum complexes containing Pt–O bonds has been reported previously. This paper reports the standard enthalpies of formation of a series of crystalline diamine(dicarboxylato)platinum(II) complexes and of bis(pentane-2,4-dionato)platinum(II). These compounds are hydrolysed quantitatively in aqueous hydrochloric acid with replacement of the Pt–O bonds by Pt–Cl, hence solution reaction calorimetry was selected for the experimental method. The standard enthalpies of formation are related to those of the $[PtCl_2(NH_2R)_2]$ (R = H, Me, or Pr^i) and $[PtCl_2(en)]$ (en = ethylenediamine) complexes which were recently determined by high-temperature microcalorimetric studies.[1]

Experimental

The calorimeter and auxiliary equipment have been described.[2] As platinum compounds are available in only small quantities, it is important that the calorimeter temperature be measured with high sensitivity. The quartz thermometer previously used discriminated to 10^{-4} K; this was replaced by a thermistor discriminating to 10^{-5} K. The average thermistor resistance over 30-s periods was measured by a Solartron digital voltmeter model 7065, then transferred to a microcomputer for storage and processing of the temperature–time data. The calorimeter was calibrated electrically for each experiment. The accuracy was checked by measuring the enthalpy of solution of tris(hydroxymethyl)methylamine in aqueous hydrochloric acid (0.1 mol dm^{-3}). The result, -29.771 ± 0.28 kJ mol^{-1}, agrees with that of Kilday and Prosen[3] (-29.770 ± 0.31 kJ mol^{-1}).

Materials.—The diamine(dicarboxylato)platinum(II) complexes were synthesized and purified by established methods,[4,5] and bis(pentane-2,4-dionato)platinum(II) as reported by Werner.[6] The compounds were characterized by elemental analysis, i.r. and ^{1}H n.m.r. spectra. The samples of $[PtCl_2(NH_2R)_2]$ were the same as used for the microcalorimetric studies.[1] The dicarboxylic acids were commercial products, purified by crystallization and sublimation *in vacuo*. The following abbreviations have been used: ethylenediamine, en; malonic acid, H_2mal; methylmalonic acid, H_2memal; ethylmalonic acid, H_2etmal; hydroxymalonic acid, H_2hmal; cyclobutane-1,1-dicarboxylic acid, H_2cbda-1,1; cyclobutane-1,2-dicarboxylic acid, H_2cbda-1,2; and pentane-2,4-dione, Hpd.

Results

Diamine(dicarboxylato)platinum(II) complexes dissolve in aqueous hydrochloric acid with quantitative replacement of the dicarboxylato-group by chlorine. The thermochemical reaction for determining the enthalpies of formation of the diamine(dicarboxylato)platinum(II) complexes is given by equation (A). The standard enthalpy of this reaction, $\Delta H^\ominus$(A),

$$[Pt\{(O_2C)_2CHR'\}(NH_2R)_2](c) + 2HCl(5\ mol\ dm^{-3}) \longrightarrow [PtCl_2(NH_2R)_2](c) + R'CH(CO_2H)_2(c) \quad (A)$$

was determined by measuring the enthalpy of solution of each reactant and product in the calorimetric solvent (HCl, 5 mol dm^{-3}) so that the final solution resulting from dissolution of the reactants was of the same composition as that from dissolution of the products. The thermochemical reaction for determining the enthalpy of formation of $[Pt(pd)_2]$ is shown by equation (B), where the calorimetric solvent was HCl

$$[Pt(pd)_2](c) + 2HCl(aqueous\ acetone) \longrightarrow PtCl_2(c) + 2Hpd(l) \quad (B)$$

(10 mol dm^{-3})–acetone (1 : 1 v/v). The standard enthalpy of reaction, $\Delta H^\ominus$(B), was determined in a fashion similar to that for $\Delta H^\ominus$(A). The enthalpies of reaction and solution are listed in Tables 1, 2, and 3 where in accord with normal thermochemical practice, the errors assigned are uncertainty intervals, *i.e.* twice the standard deviation of the mean.

The enthalpies of the thermochemical reactions (A) and (B) were then derived from the data in Tables 1, 2, and 3 using $\Delta H^\ominus(A) = \Delta H(1) - \Delta H(2) - \Delta H(3)$ or $\Delta H^\ominus(B) = \Delta H(1) -$

$\Delta H(2) - 2\Delta H(3)$ and the results are given in Table 4. The standard enthalpies of formation, $\Delta H_f^{\ominus}$, of the crystalline complexes are also given in Table 4 and were derived from the enthalpies of the thermochemical reactions and from the following auxiliary data consisting of the enthalpies of formation at 298.15 K in kJ mol^{-1}: $[PtCl_2(en)](c)$ [1] − 437 ± 7; $[PtCl_2(NH_3)_2](c)$ [1] − 467 ± 3; $[PtCl_2(NH_2Me)_2](c)$ [1] − 424 ± 8; $[PtCl_2(NH_2Et)_2](c)$ − 490 ± 10 {estimated by comparison of $\Delta H_f^{\ominus}$ for $[PtI_2(NH_2R)_2](c)$ complexes with $\Delta H_f^{\ominus}$ for $[PtCl_2(NH_2R)_2](c)$ complexes [1]}; $[PtCl_2(NH_2Pr^i)_2](c)$ [1] − 599 ± 6; $PtCl_2(c)$ [7,8] − 140.6 ± 4.0; Hpd(l) [9] − 425.5 ± 1.0; HCl (in 5 mol dm^{-3} HCl) [10] − 160.17 ± 0.01; HCl [HCl(10 mol dm^{-3})-acetone (1 : 1 v/v)] [11] − 159.17 ± 0.22.

The enthalpies of formation of the dicarboxylic acids in the crystalline and gaseous states are given in Table 5. The enthalpies of sublimation, $\Delta H_s^{\ominus}$, were measured by the 'vacuum sublimation' drop microcalorimetric method.[12] Samples (*ca.* 5 mg) were dropped into the Calvet High-Temperature Microcalorimeter, held at *ca.* 430 K, and then removed from the calorimeter by vacuum sublimation. The observed enthalpies $[H^{\ominus}(g, 430\ K) - H^{\ominus}(c, 298\ K)]$ were corrected to 298 K using values of $H^{\ominus}(g, 430\ K) - H^{\ominus}(g, 298\ K)$ estimated by a group additivity method based on data given for various carboxylic acids by Stull *et al.*[13] The microcalorimeter was calibrated *in situ* for these measurements by making use of the known enthalpies of sublimation of naphthalene and iodine. The enthalpies of formation of the crystalline compounds were derived from enthalpies of combustion; the combustion calorimeter and technique have been described.[14,15] The calorimeter was calibrated using benzoic acid (B.D.H. thermochemical standard). The mass of compound burned in each experiment was determined from the mass of carbon dioxide produced. The observed energy of combustion was converted to the standard enthalpy of combustion at 298.15 K by the method of Hubbard *et al.*[16] The standard enthalpies of formation were calculated using $\Delta H_f^{\ominus}(CO_2,g) = -393.51 \pm 0.13$ and $\Delta H_f^{\ominus}(H_2O,l) = -285.83 \pm 0.04$ kJ mol^{-1}.[17] The enthalpies of formation of gaseous methylmalonic acid and cyclobutane-1,2-dicarboxylic acid were estimated by applying the Allen bond-energy scheme using parameters derived previously for carboxylic acids,[18] and the enthalpy of formation of the crystalline compound then derived using the measured enthalpy of sublimation.

Discussion

The mean platinum–oxygen bond dissociation enthalpy in $[Pt(pd)_2]$ may be defined as $\frac{1}{4}$ of the enthalpy of the disruption reaction, $[Pt(pd)_2](g) \longrightarrow Pt(g) + 2pd(g)$, giving equation (C).

Table 1. Enthalpies of reaction of diamine(dicarboxylato)platinum(II) complexes in HCl (5 mol dm^{-3}), and of $[Pt(pd)_2]$ in HCl (10 mol dm^{-3})-acetone (1 : 1 v/v) at 298.15 K

Complex	No. of expts.	$\Delta H(1)$/kJ mol^{-1}
$[Pt(mal)(en)]$	4	−4.52 ± 0.32
$[Pt(memal)(NH_2Et)_2]$	3	−0.71 ± 0.04
$[Pt(etmal)(NH_3)_2]$	4	15.17 ± 0.27
$[Pt(etmal)(NH_2Et)_2]$	3	−18.91 ± 0.31
$[Pt(hmal)(NH_3)_2]$	4	17.42 ± 0.40
$[Pt(cbda\text{-}1,1)(NH_3)_2]$	4	10.78 ± 0.26
$[Pt(cbda\text{-}1,1)(NH_2Me)_2]$	3	7.97 ± 0.82
$[Pt(cbda\text{-}1,1)(NH_2Et)_2]$	2	−2.96 ± 0.25
$[Pt(cbda\text{-}1,1)(NH_2Pr^i)_2]$	3	−6.60 ± 0.18
$[Pt(cbda\text{-}1,2)(NH_2Me)_2]$	2	−63.12 ± 0.25
$[Pt(pd)_2]$	3	26.52 ± 0.02

Table 2. Enthalpies of solution of diamine platinum dichlorides in HCl (5 mol dm^{-3}) and of $PtCl_2$ in HCl (10 mol dm^{-3})-acetone (1 : 1 v/v) at 298.15 K

Complex	No. of expts.	$\Delta H(2)$/kJ mol^{-1}
$[PtCl_2(NH_3)_2]$	3	19.77 ± 0.25
$[PtCl_2(NH_2Me)_2]$	3	23.09 ± 0.50
$[PtCl_2(NH_2Et)_2]$	3	5.64 ± 0.30
$[PtCl_2(NH_2Pr^i)_2]$	2	−2.13 ± 0.44
$[PtCl_2(en)]$	3	9.76 ± 0.50
$PtCl_2$	3	0.45 ± 0.18

Table 3. Enthalpies of solution of dicarboxylic acids in HCl (5 mol dm^{-3}) and of pentane-2,4-dione in HCl (10 mol dm^{-3})-acetone (1 : 1 v/v) at 298.15 K

Compound	No. of expts.	$\Delta H(3)$/kJ mol^{-1}
Malonic acid (c)	4	19.33 ± 0.07
Methylmalonic acid (c)	3	18.51 ± 0.15
Ethylmalonic acid (c)	3	17.14 ± 0.11
Hydroxymalonic acid (c)	4	19.35 ± 0.07
Cyclobutane-1,1-dicarboxylic acid (c)	3	13.93 ± 0.18
Cyclobutane-1,2-dicarboxylic acid (c)	2	17.20 ± 0.05
Pentane-2,4-dione (l)	3	5.95 ± 0.05

Table 4. Enthalpies of the thermochemical reactions ($\Delta H_r^{\ominus}$) and $\Delta H_f^{\ominus}$ of the crystalline complexes at 298.15 K

Complex	$\Delta H_r^{\ominus}$/kJ mol^{-1}	$\Delta H_f^{\ominus}$/kJ mol^{-1}
$[Pt(mal)(en)]$	−33.61 ± 0.60	−974 ± 7
$[Pt(memal)(NH_2Et)_2]$	−24.86 ± 0.34	−1 087 ± 10
$[Pt(etmal)(NH_3)_2]$	−21.74 ± 0.38	−1 080 ± 3
$[Pt(etmal)(NH_2Et)_2]$	−41.69 ± 0.45	−1 083 ± 10
$[Pt(hmal)(NH_3)_2]$	−21.70 ± 0.48	−1 193 ± 3
$[Pt(cbda\text{-}1,1)(NH_3)_2]$	−22.92 ± 0.40	−959 ± 3
$[Pt(cbda\text{-}1,1)(NH_2Me)_2]$	−29.05 ± 0.98	−910 ± 8
$[Pt(cbda\text{-}1,1)(NH_2Et)_2]$	−25.53 ± 0.43	−983 ± 10
$[Pt(cbda\text{-}1,1)(NH_2Pr^i)_2]$	−18.40 ± 0.51	−1 095 ± 6
$[Pt(cbda\text{-}1,2)(NH_2Me)_2]$	−103.41 ± 0.56	−852 ± 8
$[Pt(pd)_2]$	14.17 ± 0.21	−687 ± 5

Table 5. Enthalpies of formation [a] of dicarboxylic acids at 298.15 K in kJ mol^{-1}

Compound	$\Delta H_f^{\ominus}(c)$	$\Delta H_s^{\ominus}$	$\Delta H_f^{\ominus}(g)$
Malonic acid	−890.9 ± 0.3 [b]	105.1 ± 0.8	−785.8 ± 0.9
Methylmalonic acid	[−942.5 ± 2.1]	113.2 ± 0.4	[−829.3 ± 2.0]
Ethylmalonic acid	−955.3 ± 1.0	105.5 ± 0.5	−849.8 ± 1.1
Hydroxymalonic acid	−1 068.4 ± 1.4	116.4 ± 0.3	−952.0 ± 1.5
Cyclobutane-1,1-dicarboxylic acid	−835.7 ± 1.0	111.2 ± 0.7	−724.5 ± 1.2
Cyclobutane-1,2-dicarboxylic acid	[−852.6 ± 2.2]	120.0 ± 0.9	[−732.6 ± 2.0]

[a] Values in square brackets are estimated. [b] Ref. 18.

Table 6. Enthalpies of disruption of the gaseous complexes at 298.15 K and $\bar{D}$(Pt–N), $\bar{D}$(Pt–O) in kJ mol^{-1}

Complex	$\Delta H_d^\ominus$	$\bar{D}$(Pt–N) *	$\bar{D}$(Pt–O)
[Pt(cbda-1,1)(NH$_3$)$_2$]	968	97	387
[Pt(cbda-1,1)(NH$_2$Me)$_2$]	965	108	375
[Pt(cbda-1,1)(NH$_2$Et)$_2$]	989	113	382
[Pt(cbda-1,1)(NH$_2$Pr^i)$_2$]	1 029	118	397
[Pt(memal)(NH$_2$Et)$_2$]	988	113	381
[Pt(etmal)(NH$_3$)$_2$]	964	97	385
[Pt(etmal)(NH$_2$Et)$_2$]	968	113	371
[Pt(hmal)(NH$_3$)$_2$]	975	97	391
[Pt(en)(mal)]	996	118	380
[Pt(cbda-1,2)(NH$_2$Me)$_2$]	859	108	322

* Ref. 1.

$$\bar{D}(\text{Pt–O})_{\text{pd}} = \tfrac{1}{4}[\Delta H_f^\ominus(\text{Pt,g}) + 2D(\text{O–H, Hpd, enol}) - 2\Delta H_f^\ominus(\text{H, g}) + 2\Delta H_f^\ominus(\text{Hpd, enol, g}) - \Delta H_f^\ominus\{[\text{Pt(pd)}_2], \text{c}\} - \Delta H_s^\ominus\{[\text{Pt(pd)}_2], \text{c}\}] \quad \text{(C)}$$

$\Delta H_s^\ominus\{[Pt(pd)_2], c\}$ was measured using the high-temperature microcalorimeter and was equal to 114.4 ± 2.0 kJ mol^{-1}; $\Delta H_f^\ominus$(Pt, g) [19] = 565.7 ± 4.0; $\Delta H_f^\ominus$(H, g) = 218.00 ± 0.01,[17] and $\Delta H_f^\ominus$(Hpd, enol, g) = −384.4 ± 1.3 kJ mol^{-1}.[9] Values have been proposed for D(O–H, Hpd, enol) ranging from 430 to 365 kJ mol^{-1}; Cavell *et al.*[20] from recent evidence have reassessed this value as 400 ± 20 kJ mol^{-1}. Substituting the above values in equation (C) gives $\bar{D}(\text{Pt–O})_{\text{pd}}$ = 183.4 ± 10.1 kJ mol^{-1}.

The enthalpy of disruption, $\Delta H_d^\ominus$, of a diamine(dicarboxylato)platinum(II) complex according to equation (D) can be

$$[\text{Pt}\{(\text{O}_2\text{C})_2\text{CHR}'\}(\text{NH}_2\text{R})_2](\text{g}) \longrightarrow 2\text{NH}_2\text{R(g)} + \text{Pt(g)} + \text{R}'\text{CH}(\text{CO}_2)_2\text{(g)} \quad \text{(D)}$$

equated to twice the sum of the mean bond dissociation enthalpies, *i.e.* 2[$\bar{D}$(Pt–O) + $\bar{D}$(Pt–N)], and $\Delta H_d^\ominus$ is given by equation (E). To derive $\Delta H_d^\ominus$ the following auxiliary

$$\Delta H_d^\ominus = 2\Delta H_f^\ominus(\text{NH}_2\text{R, g}) + \Delta H_f^\ominus(\text{Pt, g}) + \Delta H_f^\ominus[\text{R}'\text{CH}(\text{CO}_2)_2\text{, g}] - \Delta H_f^\ominus\{[\text{Pt}(\text{O}_2\text{C})_2\text{CHR}'\}(\text{NH}_2\text{R})_2]\text{, g}\} \quad \text{(E)}$$

data of the enthalpies of formation at 298.15 K in kJ mol^{-1} were required: NH$_3$(g) = −45.9 ± 0.4; [17] NH$_2$Me(g) = −23.0 ± 0.4; [18] NH$_2$Et(g) = −47.5 ± 0.7; [18] NH$_2$Pr^i(g) = −83.8 ± 0.5; [18] ethylenediamine(g) = −17.8 ± 2.1. [15] For $\Delta H_f^\ominus[\text{R}'\text{CH}(\text{CO}_2)_2\text{, g}]$ an estimation of $\Delta H^\ominus$ for the dissociation, $\text{R}'\text{CH}(\text{CO}_2\text{H})_2\text{(g)} \longrightarrow 2\text{H(g)} + \text{R}'\text{CH}(\text{CO}_2)_2\text{(g)}$, is required. It is assumed that this is 2D(CH$_3$CO$_2$–H) plus a contribution of 40 kJ mol^{-1} for the internal hydrogen bond in the malonic acid derivatives. Cook and Taylor [21] reported D(CH$_3$CO$_2$–H) = 423 ± 10 kJ mol^{-1}, hence for the malonic acid derivatives, $\Delta H^\ominus$(dissociation) = 886 kJ mol^{-1}. In cyclobutane-1,2-dicarboxylic acid, however, an internal hydrogen bond is not expected hence $\Delta H^\ominus$(dissociation) = 846 kJ mol^{-1}. Attempts to measure $\Delta H_s^\ominus$ of these complexes in the microcalorimeter failed because of decomposition at elevated temperatures. There is no basis for differentiating between the various complexes so we assume a constant value of $\Delta H_s^\ominus$ of 190 kJ mol^{-1} from comparison with other molecules of comparable size and molecular weight. The enthalpies of disruption are given in Table 6, together with $\bar{D}$(Pt–N) from the [PtCl$_2$(NH$_2$R)$_2$] complexes [1] and the derived value of $\bar{D}$(Pt–O).

In view of the uncertainties associated with the estimations no correlation of $\bar{D}$(Pt–O) with structure of the malonic acid ligand can be attempted; the average $\bar{D}$(Pt–O) in these complexes is 380 ± 20 kJ mol^{-1}, close to $D_{298}^\ominus$(Pt–O) = 372.5 kJ mol^{-1} in the PtO gaseous molecule.[22] The reduction of $\bar{D}$(Pt–O) in [Pt(cbda-1,2)(NH$_2$Me)$_2$] is significant, however, and arises because the Pt–O bonds in this complex participate in a seven-membered ring for which an excess of strain energy is expected compared with the other complexes in which the corresponding ring is six-membered.

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