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Standard molar enthalpy of formation of crystalline dicarbonylbiscyclopentadienyltitanium(II)

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Abstract

The standard ($p^0 = 0.1$ MPa) molar enthalpy of formation, at 298.15 K, of crystalline dicarbonylbiscyclopentadienyltitanium(II), $Ti(\eta\text{-}C_5H_5)_2(CO)_2$, has been derived from the enthalpy of the oxidative reaction of $Ti(\eta\text{-}C_5H_5)_2(CO)_2$ with 9,10-phenanthraquinone in toluene determined by precision solution-reaction calorimetry) as ΔH_f^0 $\{Ti(\eta\text{-}C_5H_5)_2(CO)_2, cr\} = -371.5 \pm 12.9$ kJ mol^{-1}. A re-evaluation of the Ti–CO bond enthalpy term and an estimate of the mean bond dissociation enthalpy are also described.

Introduction

Discarbonylbiscyclopentadienyltitanium(II), $Ti(\eta\text{-}C_5H_5)_2(CO)_2$, is the most widely studied titanium(II) dicarbonyl complex. It can be isolated as dark red crystals by crystallization from toluene or by sublimation. The crystal structure [1] shows it possesses almost exact C_{2v} symmetry, with a Ti–C(carbonyl) bond length of 2.03 Å, and that the distance from the titanium to the center of the cyclopentadienyl ligands (2.025 Å) is shorter than that in Ti^{IV} complexes. The IR spectrum has also been assigned [2]. $Ti(\eta\text{-}C_5H_5)_2(CO)_2$ is a very reactive compound, much used in the preparation of other bent titanocenes. All its reactions are characterized by the loss of at least one coordinated carbon monoxide and oxidation of Ti^{II} to higher oxidation states. Recently, titanocene derivatives have been studied [3–5] as antitumor agents.

The importance of the chemistry of $Ti(\eta\text{-}C_5H_5)_2(CO)_2$, prompted us to investigate its thermochemistry.

Experimental

Calorimeter

The reaction and solution enthalpies were measured in a reaction-solution calorimeter with an all glass reaction vessel, similar in design to other calorimeters

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previously described [6–8]. Some other important details of the technique used have been reported elsewhere [8,9]. To ensure an inert atmosphere in the calorimeter vessel, pure dry nitrogen was bubbled through the solvent for about 30 minutes before each run, and the glass bulbs containing the samples for the calorimetric runs were sealed under nitrogen.

Compounds

$Ti(\eta\text{-}C_5H_5)_2(CO)_2$ was prepared as described in ref. 10 and purified by sublimation in vacuo. $Ti(\eta\text{-}C_5H_5)_2(O_2C_{14}H_8)$ was prepared, from $Ti(\eta\text{-}C_5H_5)_2(CO)_2$, by a published method [11] and crystallised out from the reaction mixture upon addition of heptane. A commercial sample (Janssen Chimica) 9,10-phenanthraquinone ($C_{14}H_8O_2$) was purifed by repeated sublimation in vacuo. All compounds were characterized by elemental analysis and IR spectroscopy.

Toluene (B.D.H., AnalaR) used as calorimetric solvent was dried over metallic sodium, distilled, and stored in the dark over metallic sodium and under nitrogen.

Reaction

The oxidative reaction of dicarbonylbiscyclopentadienyltitanium(II), $Ti(\eta\text{-}C_5H_5)_2(CO)_2$, with 9,10-phenanthraquinone in toluene, as described by Floriani and Fachinetti [11], was used as the calorimetric reaction to provide the information needed to derive the standard molar enthalpy of formation of the $Ti(\eta\text{-}C_5H_5)_2(CO)_2$ in the crystal state:

$$Ti(\eta\text{-}C_5H_5)_2(CO)_2(cr) + C_{14}H_8O_2(cr) \rightarrow Ti(\eta\text{-}C_5H_5)_2(O_2C_{14}H_8)(cr) + 2CO(g) \qquad (1)$$

Results

The standard enthalpy change of reaction 1, ΔH_R, was determined indirectly, from ΔH_1, ΔH_2, ΔH_3 and ΔH_4, the enthalpies of the stepwise solution of reactants and products, in stoichiometric ratio, in the calorimetric solvent (toluene). These solution enthalpies, are listed in Table 1 as the mean values from at least five independent experiments at 298.15 K; the associated uncertainties are twice the standard deviations of the means. ΔH_3, the enthalpy of dissolution of the gaseous carbon monoxide in toluene (solvent) is taken as zero under our conditions, since it is known [12] that the mole fraction of CO in toluene (at 1 atm of partial pressure

Table 1

Enthalpies of solution and reaction at 298.15 K

Reaction	Number of experiments	ΔH_i/kJ mol^{-1}
$C_{14}H_8O_2$ (cr) + toluene → solution 1	5	$\Delta H_1 = 22.39 \pm 0.29$
$Ti(\eta\text{-}C_5H_5)_2(CO)_2$ (cr) + solution 1 → solution 2	5	$\Delta H_2 = -29.27 \pm 0.82$
CO(g) + toluene = toluene	–	$\Delta H_3 = 0$
$Ti(\eta\text{-}C_5H_5)_2(O_2C_{14}H_8)$ (cr) + toluene → solution 3	5	$\Delta H_4 = 10.62 \pm 0.40$
solution 2 + solution 3	3	$\Delta H_5 = 0.00 \pm 0.02$

and 298.15 K) is 8.02×10^{-4} and the enthalpy of solution under these conditions only 1.26 kJ mol^{-1} so that under the conditions of our calorimetric experiments the enthalpy of solution of the small amount of carbon monoxide evolved can be neglected, since it is much smaller than the experimental errors associated with the calorimetric measurements.

The standard enthalpy of reaction 1 is related to the stepwise solution-reaction enthalpies, through equation 2:

$$\Delta H_R = \Delta H_1 + \Delta H_2 - 2\Delta H_3 - \Delta H_4 + \Delta H_5 = -17.5 \pm 1.0 \text{ kJ mol}^{-1} \tag{2}$$

The standard molar enthalpy of formation of the crystalline $\mathrm{Ti}(\eta\text{-}C_5H_5)_2(CO)_2$ was derived from the above enthalpy of reaction, (ΔH_R), and the following auxiliary data:

$\Delta H_f^0(C_{14}H_8O_2, \mathrm{cr}) = -154.7 \pm 2.4$ kJ mol^{-1} [13]

$\Delta H_f^0\{\mathrm{Ti}(\eta\text{-}C_5H_5)_2(O_2C_{14}H_8), \mathrm{cr}\} = -322.6 \pm 12.7$ kJ mol^{-1} [14]

$\Delta H_f^0(\mathrm{CO, g}) = -110.525 \pm 0.001$ kJ mol^{-1} [15],

as:

$\Delta H_f^0\{\mathrm{Ti}(\eta\text{-}C_5H_5)_2(CO)_2, \mathrm{cr}\} = -371.5 \pm 12.9$ kJ mol^{-1}

Discussion

The determined standard molar enthalpy of formation of the crystalline $\mathrm{Ti}(\eta\text{-}C_5H_5)_2(CO)_2$, considered together with its enthalpy of sublimation at 298.15 K, $\Delta H^0_{\mathrm{sub.}}\{\mathrm{Ti}(\eta\text{-}C_5H_5)_2(CO)_2\} = 84.2 \pm 3.5$ kJ mol^{-1} [16], yields the standard molar enthalpy of formation of the gaseous complex: $\Delta H_f^0\{\mathrm{Ti}(\eta\text{-}C_5H_5)_2(CO)_2, \mathrm{g}\} = -287.3 \pm 13.4$ kJ mol^{-1}.

To provide a measure of the titanium–carbon (carbon monoxide) bond strengths, the bond enthalpy term, E(Ti–CO) and the mean bond dissociation enthalpy, $\bar{D}$(Ti–CO), were calculated for $\mathrm{Ti}(\eta\text{-}C_5H_5)_2(CO)_2$ from equations 3 and 4 [14]:

$$\begin{aligned} 2E(\text{Ti–CO}) = {} & 2E(\text{Ti–Cl}) + 2\Delta H_f^0(\text{CO}^\star, \text{g}) \\ & - 2\Delta H_f^0(\text{Cl, g}) - \Delta H_f^0\{\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2, \text{g}\} \\ & + \Delta H_f^0\{\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2, \text{g}\} + E\text{R}_3 - E\text{R}_1 \end{aligned} \tag{3}$$

$$\begin{aligned} 2\bar{D}(\text{Ti–CO}) = {} & 2E(\text{Ti–Cl}) + 2\Delta H_f^0(\text{CO, g}) \\ & - 2\Delta H_f^0(\text{Cl, g}) - \Delta H_f^0\{\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_2, \text{g}\} \\ & + \Delta H_f^0\{\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2, \text{g}\} + E\text{R}_3 \end{aligned} \tag{4}$$

In line with the usage in ref. 14, CO* in these equations denotes the non-reorganized CO ligand and $E\mathrm{R}_1$ and $E\mathrm{R}_3$ represent the reorganization energies of the moieties $\mathrm{Ti}(\eta\text{-}C_5H_5)_2$, respectively, from the complex $\mathrm{Ti}(\eta\text{-}C_5H_5)_2(CO)_2$, and from the dichloride $\mathrm{Ti}(\eta\text{-}C_5H_5)_2Cl_2$. E(Ti–Cl), is the bond enthalpy term in the dichloride complex, and is taken as 430.5 ± 1.3 kJ mol^{-1} [17], as discussed previously [14].

The reorganization energies $E\mathrm{R}_1$ and $E\mathrm{R}_3$ can be estimated by use of results from extended Hückel calculations, and were taken [16] as $E\mathrm{R}_1 = 0$ kJ mol^{-1} and

$ER_3 = -11$ kJ mol^{-1}. The reorganization energy of $CO^{\star}$ was estimated by MINDO/3 calculations [18] from curves relating CO energy with C–O bond lengths as $ER_{CO} = -2$ kJ mol^{-1}, by use of the knowledge that the C–O bond lengths in $Ti(\eta\text{-}C_5H_5)_2(CO)_2$, and in the free CO are 115 pm [1] and 112.8 pm [19], respectively.

By use of the above values, and of the following auxiliary data: $\Delta H_f^0\{Ti(\eta\text{-}C_5H_5)_2Cl_2, g\} = -266.0 \pm 8.9$ kJ mol^{-1} [17] and $\Delta H_f^0(Cl, g) = 121.30 \pm 0.01$ kJ mol^{-1} [17], and bearing in mind that

$$\Delta H_f^0(CO^{\star}, g) = \Delta H_f^0(CO, g) - ER_{CO} \qquad (5)$$

we derive from equations 3 and 4 the following values: $E(Ti\text{–}CO) = 206 \pm 8$ kJ mol^{-1}, and $\bar{D}(Ti\text{–}CO) = 204 \pm 8$ kJ mol^{-1}.

Despite the large number of thermochemical studies involving transition metal carbonyls, no data have been reported previously for the energetics of the Ti–CO bond.

For the hexacarbonyls of Mo and W, $\bar{D}(M\text{–}CO) = 152$ and 180 kJ mol^{-1}, respectively [21], and the order $\bar{D}(Mo\text{–}CO) < \bar{D}(W\text{–}CO) < \bar{D}(Ti\text{–}CO)$, is also observed for the corresponding metal–oxygen, metal–sulfur, metal–halogen, metal–hydrogen and metal–alkyl mean bond dissociation enthalpies in MCp_2L_2 complexes [14].

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