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ENTHALPIES OF FORMATION OF Ti(η-C_5H_5)$_2$$L_2$ COMPLEXES (L = 3-$CH_3C_6H_4$, 4-$CH_3C_6H_4$, 4-$CF_3C_6H_4$, AND 4-$CH_3OC_6H_4$)

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Summary

The standard enthalpies of formation of the Ti(η-C_5H_5)$_2$$L_2$ crystalline complexes at 298.15 K have been determined by reaction-solution calorimetry. The results gave ΔH_f°[Ti(η-C_5H_5)$_2$(3-$CH_3C_6H_4$)$_2$,c] 199.0 ± 9.3 kJ mol^{-1}, ΔH_f°[Ti(η-C_5H_5)$_2$(4-$CH_3C_6H_4$)$_2$,c] 201.8 ± 9.5 kJ mol^{-1}, ΔH_f°[Ti(η-C_5H_5)$_2$(4-$CF_3C_6H_4$)$_2$,c] − 1110.4 ± 8.2 kJ mol^{-1}, and ΔH_f°[Ti(η-C_5H_5)$_2$(4-$CH_3OC_6H_4$)$_2$,c] − 59.6 ± 8.4 kJ mol^{-1}. The titanium–carbon mean bond dissociation enthalpies, $\bar{D}$(Ti–C), and bond enthalpy terms, E(Ti–C), were also evaluated.

Introduction

We recently reported thermochemical data for the complexes Ti(η-C_5H_5)$_2$$Ph_2$ and Ti(η-C_5H_5)$_2$$Fc_2$ (Ph = C_6H_5 and Fc = (η-C_5H_5)Fe(η-C_5H_4)) [1]. The values obtained for the titanium–carbon bond enthalpy terms, E(Ti–C), indicate similar Ti–Ph and Ti–Fc "bond strengths". The present paper extends the studies to other Ti(η-C_5H_5)$_2$$L_2$ complexes containing titanium–carbon σ bonds, and deals with the effects of ring substituents (3-CH_3, 4-CH_3, 4-CF_3 and 4-CH_3O) on the bond enthalpy terms E(Ti–L).

Early results for E(Ti–OR) in Ti(η-C_5H_5)$_2$(OR)$_2$ complexes (R = C_6H_5, 2-$CH_3C_6H_4$, 3-$CH_3C_6H_4$, 4-$CH_3C_6H_4$ and 2-ClC_6H_4) [2] suggest that the titanium–phenyl ring bond enthalpy terms should be fairly insensitive to the position and the nature of the substituent. This being so then the results for E(Ti–L) should be close to E(Ti–Ph), thus providing an indirect confirmation of this value.

Experimental

The reaction and solution enthalpies were measured in the reaction-solution calorimeter previously described [3]. The thermochemical measurements were not made under nitrogen since all the compounds are unaffected by exposure for short periods to air or moisture.

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Compounds

Complexes $Ti(\eta\text{-}C_5H_5)_2(3\text{-}CH_3C_6H_4)_2$, $Ti(\eta\text{-}C_5H_5)_2(4\text{-}CH_3C_6H_4)_2$, $Ti(\eta\text{-}C_5H_5)_2(4\text{-}CF_3C_6H_4)_2$ and $Ti(\eta\text{-}C_5H_5)_2(4\text{-}CH_3OC_6H_4)_2$ were prepared, purified and characterized as described in the literature [4,5]. The reaction solutions were prepared from Merck p.a. hydrochloric acid and acetone, which were used without any further purification. Spectroscopically pure Merck toluene was also used. Aldrich α,α,α-trifluorotoluene and Merck anisol were purified as described by Perrin et al. [6].

Reactions

The solvent used in the thermochemical studies of reaction 1 was a 1/4 mixture of 10.0 mol dm^{-3} aqueous hydrochloric acid and acetone. The thermochemical disadvantages of this mixture were discussed in a previous paper [7].

$$Ti(\eta\text{-}C_5H_5)_2L_2\ (c) + 2HCl\ (soln) \rightarrow Ti(\eta\text{-}C_5H_5)_2Cl_2\ (soln) + 2LH\ (soln) \qquad (1)$$

All the reactions were found to be fast and quantitative, and the products were confirmed by IR spectroscopic analysis.

All the reactions and solution enthalpies are mean values from at least five independent experiments and are referred to 298.15 K. The associated uncertainties are twice the standard deviations of those means.

Auxiliary data

The following standard enthalpies of formation and enthalpies of vaporization at 298 K were used in evaluating the thermochemical results (values in kJ mol^{-1}): ΔH_f°(HCl, soln) -172.59 ± 0.51 [7]; $\Delta H_f^\circ(C_6H_5CH_3$, l) 12.1 ± 0.3 [8]; $\Delta H_f^\circ(C_6H_5CF_3$, l) -636.6 ± 0.9 [8]; $\Delta H_f^\circ(C_6H_5CH_3O$, l) -114.8 ± 0.7; $\Delta H_f^\circ[Ti(\eta\text{-}C_5H_5)_2Cl_2$, c] -383.2 ± 7.5 [9]; $\Delta H_v^\circ(C_6H_5CH_3)$ 37.99 ± 0.04 [10]; $\Delta H_v^\circ(C_6H_5CF_3)$ 37.6 ± 0.1 [8]; $\Delta H_v^\circ(C_6H_5CH_3O)$ 46.8 ± 0.2 [8]; $\Delta H_s^\circ[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ 118.8 ± 2.1 [9]; ΔH_f°(Cl, g) 121.302 ± 0.008 [11]; ΔH_f°(H, g) 217.997 ± 0.006 [11].

$D(CH_3C_6H_4\text{–}H)$, $D(CF_3C_6H_4\text{–}H)$ and $D(CH_3OC_6H_4\text{–}H)$ were assumed equal to $D(C_6H_5\text{–}H)$ 464.0 ± 8.4 [12].

Calculations

The extended Hückel molecular orbital calculations were made by use of the ICON 8 program, developed by Hoffman and coworkers [13,14]. The basis set for the titanium atom consisted of $3d$, $4s$ and $4p$ orbitals. The s and p orbitals were described by single Slater-type wave functions and the d orbitals were taken as contracted linear combinations of two Slater-type wave functions [15]. The orbital exponents and the parameters for the extended Hückel calculations are collected in Table 1. All calculations were performed by using the modified Wolfsberg–Helmholz method [16].

The model compound $Ti(\eta\text{-}C_5H_5)_2(RC_6H_4)_2$ was considered as having C_{2v} symmetry, and its structure was based on that of $Ti(\eta\text{-}C_5H_5)_2Ph_2$ as determined by X-ray diffraction [17].

The Ti–(η-C_5H_5) ring distance was taken as 204.8 pm and other bond lengths are Ti–C′ 227, C–C 134, C′–C′ 139, C–C (single bond) 150, C–F 135, C–H 109, C′–H 109 pm, where C denotes a carbon atom in a cyclopentadienyl ring and C′ a carbon atom in a phenyl ring. The ring normals angle was 136° and the C′–Ti–C′ angle 97.3°.

TABLE 1

ORBITAL EXPONENTS AND PARAMETERS USED FOR THE EXTENDED HÜCKEL MOLECULAR ORBITAL CALCULATIONS

Orbital	Slater exponent	$-H_{ii}$ (eV) [a]
H 1s	1.300	13.60
C 2s	1.625	21.40
C 2p	1.625	11.40
F 2s	2.425	40.00
F 2p	2.425	18.10
Ti 4s	1.075	8.97
Ti 4p	0.675	5.44
Ti 3d	[b]	10.81

[a] 1 eV = 96.4845 kJ mol^{-1}. [b] $\zeta_1 = 4.55$; $\zeta_2 = 1.40$; $C_1 = 0.4206$; $C_2 = 0.7839$.

Results

The thermochemical results obtained are summarized in Table 2. ΔH_r denotes the enthalpy of reaction 1, ΔH_{d1} refers to the enthalpy of solution of $Ti(\eta\text{-}C_5H_5)_2Cl_2$ (c) in the solution of aqueous HCl and acetone, and ΔH_{d2} refers to the enthalpies of solution of $CH_3C_6H_5$, $CF_3C_6H_5$ or $CH_3OC_6H_5$ in the solution containing stoichiometric amounts of $Ti(\eta\text{-}C_5H_5)_2Cl_2$. The values of the standard enthalpies of formation of the crystalline complexes are presented in Table 3, and were evaluated by using the thermochemical results in Table 2 and the auxiliary data given above.

The estimated values for the enthalpies of sublimation, together with the enthalpies of formation of the gaseous complexes are also listed in Table 3.

TABLE 2

THERMOCHEMICAL RESULTS (kJ mol^{-1}) FOR REACTION 1

Complex	ΔH_r	ΔH_{d1}	ΔH_{d2}
$Ti(\eta\text{-}C_5H_5)_2(3\text{-}CH_3C_6H_4)_2$	−186.9 ± 5.2	17.2 ± 1.3	4.36 ± 0.21
$Ti(\eta\text{-}C_5H_5)_2(4\text{-}CH_3C_6H_4)_2$	−189.7 ± 5.5	17.2 ± 1.3	4.36 ± 0.21
$Ti(\eta\text{-}C_5H_5)_2(4\text{-}CF_3C_6H_4)_2$	−176.8 ± 2.2	17.2 ± 1.3	3.39 ± 0.29
$Ti(\eta\text{-}C_5H_5)_2(4\text{-}CH_3OC_6H_4)_2$	−184.0 ± 3.1	17.2 ± 1.3	3.43 ± 0.21

TABLE 3

STANDARD ENTHALPIES OF FORMATION ΔH_f°(c) AND ΔH_f°(g) (kJ mol^{-1})

Complex	ΔH_f°(c)	ΔH_s° [a]	ΔH_f°(g)
$Ti(\eta\text{-}C_5H_5)_2(3\text{-}CH_3C_6H_4)_2$	199.0 ± 9.3	95 ± 8	294.0 ± 12.3
$Ti(\eta\text{-}C_5H_5)_2(4\text{-}CH_3C_6H_4)_2$	201.8 ± 9.5	95 ± 8	296.8 ± 12.4
$Ti(\eta\text{-}C_5H_5)_2(4\text{-}CF_3C_6H_4)_2$	−1110.4 ± 8.2	110 ± 8	−1000.4 ± 11.5
$Ti(\eta\text{-}C_5H_5)_2(4\text{-}CH_3OC_6H_4)_2$	−59.6 ± 8.4	104 ± 8	44.4 ± 11.6

[a] Estimated values.

Discussion

The titanium carbon mean bond dissociation enthalpies, $\bar{D}$(Ti–L), shown in Table 4, were calculated by use of an equation equivalent to eq. 2 [2,18], using the experimental results of Table 2 and the auxiliary data given above.

$$\bar{D}(\text{Ti–L}) = E(\text{Ti–Cl}) + \Delta H_f^\circ(\text{L, g}) - \Delta H_f^\circ(\text{Cl, g}) - \{\Delta H_f^\circ[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{L}_2,\text{g}] - \Delta H_f^\circ[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2,\text{g}]\}/2 + ER_3/2 \tag{2}$$

E(Ti–Cl), the bond enthalpy term in Ti(η-C_5H_5)$_2$Cl$_2$, was taken as 430.5 ± 1.3 kJ mol^{-1} [2,9,18]. ER_3 is the reorganization enthalpy of the fragment Ti(η-C_5H_5)$_2$ from the dichloride complex. Its value, ca. −10 kJ mol^{-1}, was obtained by using extended Hückel molecular orbital calculations described in a previous communication [19].

The titanium–carbon bond enthalpy terms, E(Ti–L), shown in Table 3, were determined by an equation equivalent to eq. 3, where $\Delta H_f^\circ(\text{L}^\star, \text{g})$ denotes the enthalpy of formation of the unreorganized ligand and ER_1 is the enthalpy of reorganization of the Ti(η-C_5H_5)$_2$ moiety from the complex Ti(η-C_5H_5)$_2$L$_2$.

$$E(\text{Ti–L}) = E(\text{Ti–Cl}) + \Delta H_f^\circ(\text{L}^\star,\text{g}) - \Delta H_f^\circ(\text{Cl, g}) - \{\Delta H_f^\circ[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{L}_2,\text{g}] - \Delta H_f^\circ[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2,\text{g}]\}/2 + (ER_3 - ER_1)/2 \tag{3}$$

ER_1 cannot be evaluated since the molecular structures of the four complexes Ti(η-C_5H_5)L$_2$ are unknown. However it seems reasonable to assume that the angles (η-C_5H_5)–Ti–(η-C_5H_5) in those molecules and in Ti(η-C_5H_5)$_2$Ph$_2$ are similar, ca. ~ 136° [20]. Use of this angle yields a small value (about −5 kJ mol^{-1}) for the correction term $(ER_3 - ER_1)/2$ [1,19].

The unavailability of the structures of the complexes also hinders the computation of $\Delta H_f^\circ(\text{L}^\star, \text{g})$. Nevertheless, if we assume that the structures of L in the organometallic compounds and in the molecules LH are comparable, $\Delta H_f^\circ(\text{L}^\star, \text{g})$ can be easily obtained [2,18] by taking the Laidler term E(Ph–H) as 420.6(±8) kJ mol^{-1} [10].

TABLE 4

MEAN BOND DISSOCIATION ENTHALPIES AND BOND ENTHALPY TERMS (kJ mol^{-1})

Complex	$\bar{D}$(Ti–C)	E(Ti–C)
Ti(η-C_5H_5)$_2$(3-$CH_3C_6H_4$)$_2$	326 ± 10 321 [a]	283 ± 10
Ti(η-C_5H_5)$_2$(4-$CH_3C_6H_4$)$_2$	325 ± 10 320 [a]	281 ± 10
Ti(η-C_5H_5)$_2$(4-$CF_3C_6H_4$)$_2$	324 ± 10 319 [a]	281 ± 9
Ti(η-C_5H_5)$_2$(4-$CH_3OC_6H_4$)$_2$	333 ± 10 328 [a]	289 ± 9

[a] This value contain the correction term $ER_3/2$ (see text).

TABLE 5

TITANIUM–CARBON OVERLAP POPULATIONS

Complex	Overlap populations
$Ti(\eta\text{-}C_5H_5)_2(C_6H_5)_2$	0.4098
$Ti(\eta\text{-}C_5H_5)_2(3\text{-}CH_3C_6H_4)_2$	0.4100
$Ti(\eta\text{-}C_5H_5)_2(4\text{-}CH_3C_6H_4)_2$	0.4101
$Ti(\eta\text{-}C_5H_5)_2(4\text{-}CF_3C_6H_4)_2$	0.4097

The assumptions would not be generally valid for $M(\eta\text{-}C_5H_5)_2L_2$ complexes, since some ligands are stabilized to a large extent when bound to a metal atom. For example, the N_3 moiety in the complex $Ti(\eta\text{-}C_5H_5)_2(N_3)_2$ shows a remarkable decrease of the nitrogen–nitrogen bond lengths compared to those in the same fragment in HN_3, implying a large negative correction to $\Delta H_f^\circ(N_3^\star, g)$ calculated by using a bond enthalpy-bond length correlation [18]. Although it is expected that the correction is considerably smaller in the case of many-atom ligands, such as phenyl rings [18], it must be stressed that a satisfactory answer to this problem can only be provided when the molecular structures of the complexes are available. In any case the same assumption was also made for L = Ph [1], and thus the observed trend in values of E(Ti–phenyl ring) should be reliable.

The main conclusion that can be drawn from the bond enthalpy terms in Table 4 is that the nature and the position of the substituents have no significant influence on the titanium–phenyl ring bond strength. Moreover the values are close to E(Ti–Ph) ~ 271 ± 9 kJ mol^{-1} [1] (or 266 kJ mol^{-1} if the correction term $(ER_3 - ER_1)/2$ is considered) and to other titanium–carbon bond enthalpy terms reported in the literature, such as E(Ti–Fc) ~ 262 ± 11 kJ mol^{-1} [1] and $E(Ti\text{–}CH_2Ph)$ ~ 280 ± 10 kJ mol^{-1}. This latter result was recalculated from $\Delta H_f^\circ[Ti(\eta\text{-}C_5H_5)_2(CH_2Ph)_2, g]$ 279.5 ± 9.4 kJ mol^{-1} [21] and from the Laidler term E(C–H) 410.8 (±8) kJ mol^{-1} [10]. The present set of values is also comparable with E(Ti–C) in $Ti(CH_2Ph)_4$ (257 ± 12 kJ mol^{-1}) and in $Ti[CH_2Si(CH_3)_3]_4$ (262 ± 15 kJ mol^{-1}) [22]. As noted before [1,19], this is consistent with the assumption of equal titanium–chloride bond enthalpy terms in $TiCl_4$ and $Ti(\eta\text{-}C_5H_5)_2Cl_2$.

Extended Hückel molecular orbital calculations on a series of complexes involved in this study are in agreement with the observed constancy of E(Ti–phenyl ring). Those calculations, which were based on the structure of $Ti(\eta\text{-}C_5H_5)_2Ph_2$, reveal

TABLE 6

CHARGE DISTRIBUTION FOR THE PHENYL RING CARBON ATOMS

Complex	Charges	
	C(1) [a]	C(2) [b]
$Ti(\eta\text{-}C_5H_5)_2(C_6H_5)_2$	−0.387	−0.041
$Ti(\eta\text{-}C_5H_5)_2(3\text{-}CH_3C_6H_4)_2$	−0.387	0.067
$Ti(\eta\text{-}C_5H_5)_2(4\text{-}CH_3C_6H_4)_2$	−0.408	0.064
$Ti(\eta\text{-}C_5H_5)_2(4\text{-}CF_3C_6H_4)_2$	−0.396	−0.007

[a] Carbon atom coordinated to the titanium atom. [b] Carbon atom neighbour to the substituent.

that the overlap populations between the titanium atom and the adjacent carbon atom do not vary with the ring substituent (Table 5). The charge distribution in the ring is affected by the presence of the substituent, mostly at the neighbouring carbon atom (C(2) in Table 6). The charges in the remaining carbon atoms are seen to be nearly independent of the presence of that substituent, as shown in Table 6 for the carbon atom adjacent to the titanium atom (C(1) Table 6).

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