

THE PLATINUM—CARBON BOND STRENGTH IN $\text{Pt}(\text{PPh}_3)_2(\text{CH}_3)\text{I}$

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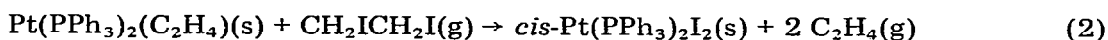
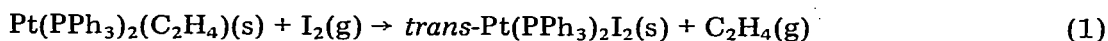
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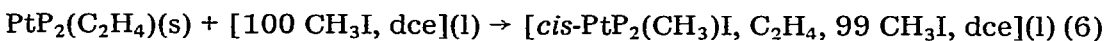
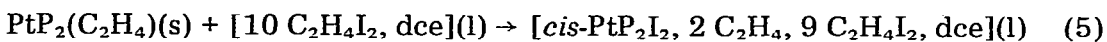
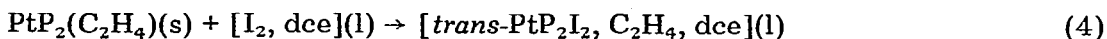
Summary

The enthalpies of reactions 1–3 have been determined

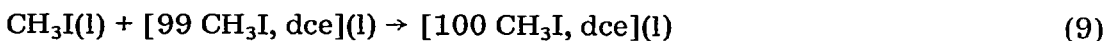
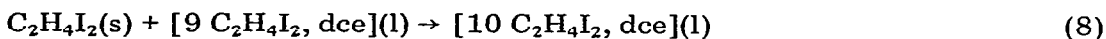


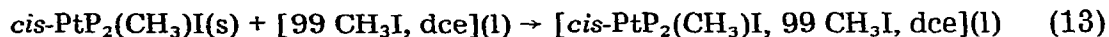
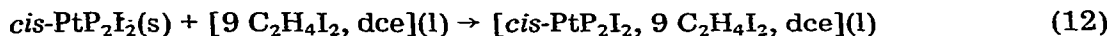
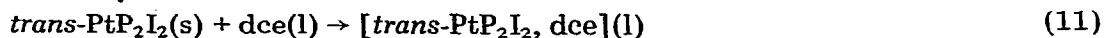
as $\Delta H(1) = -176.6 \pm 5.4$, $\Delta H(2) = -107.8 \pm 6.0$, and $\Delta H(3) = -78.9 \pm 2.0$ kJ mol⁻¹. The bond dissociation energy difference $D_1(\text{Pt}-\text{CH}_3) - D_1(\text{Pt}-\text{I}) = +6 \pm 5$ kJ mol⁻¹ is calculated, which indicates that the two bonds have very similar strengths.

Bis(triphenylphosphine)(ethylene)platinum(0), $\text{PtP}_2(\text{C}_2\text{H}_4)$, reacts rapidly and quantitatively, at 25°C, with I_2 [1], $\text{CH}_2\text{ICH}_2\text{I}$, and CH_3I [2] in 1,2-dichloroethane according to eq. 4–6, where dce represents 10⁴ mol of solvent.



Enthalpies of these reactions have been measured calorimetrically. In addition, enthalpies of the solution reactions 7–13 have also been measured.





The following values, in kJ mol^{-1} , have been obtained:

$\Delta H(4) -138.4 \pm 1.4$, $\Delta H(5) -73.9 \pm 1.0$, $\Delta H(6) -45.9 \pm 1.3$, $\Delta H(7) +22.32 \pm 0.52$, $\Delta H(8) +18.89 \pm 0.55$, $\Delta H(9) +1.21 \pm 0.03$, $\Delta H(10) -10.94 \pm 0.74$, $\Delta H(11) +9.0 \pm 1.1$, $\Delta H(12) +9.0 \pm 1.1$, $\Delta H(13) +17.4 \pm 0.48$. Incorporating the values $\Delta H(\text{sub})(\text{I}_2, \text{s}) = +62.44 \pm 0.02$ [3], $\Delta H(\text{sub})(\text{C}_2\text{H}_4\text{I}_2, \text{l}) = +65.7 \pm 4.1$, and $\Delta H(\text{vap})(\text{CH}_3\text{I}, \text{l}) = +28.03 \pm 1.3 \text{ kJ mol}^{-1}$ [4] yields the values for $\Delta H(1) - \Delta H(3)$ listed in the abstract.

Using the ΔH_f° values [4]: $\text{C}_2\text{H}_4\text{I}_2(\text{g}) +64.9 \pm 1.7$, $\text{C}_2\text{H}_4(\text{g}) +52.1 \pm 0.4 \text{ kJ mol}^{-1}$ leads to a value for the enthalpy of isomerization $\text{cis-} \rightarrow \text{trans-Pt}(\text{PPh}_3)_2\text{I}_2(\text{s})$, $-19 \pm 5 \text{ kJ mol}^{-1}$. This value is close to the $-13.4 \text{ kJ mol}^{-1}$ for the isomerization $\text{cis-} \rightarrow \text{trans-Pt}(\text{PEt}_3)_2\text{I}_2(\text{s})$ obtained by scanning calorimetry [5].

The enthalpies of reactions 1 and 3 and the enthalpy of isomerization may be used to derive the bond dissociation energy relationships

$$D(\text{Pt}-\text{C}_2\text{H}_4) + D(\text{I}-\text{I}) - D_1(\text{Pt}-\text{I}) - D_2(\text{Pt}-\text{I}) = -157.4 - W + Y \quad (14)$$

$$D(\text{Pt}-\text{C}_2\text{H}_4) + D(\text{CH}_3-\text{I}) - D_1(\text{Pt}-\text{CH}_3) - D_2(\text{Pt}-\text{I}) = -78.9 - W + Z \quad (15)$$

where W , Y and Z are the enthalpies of sublimation of $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$, $\text{cis-Pt}(\text{PPh}_3)_2\text{I}_2$ and $\text{cis-Pt}(\text{PPh}_3)_2(\text{CH}_3)\text{I}$, respectively. If $W = Y = Z$, and using the values $D(\text{I}-\text{I}) = 151.24 \pm 0.01$ [3] and $D(\text{CH}_3-\text{I}) = 236 \pm 4 \text{ kJ mol}^{-1}$ [6], we obtain the relationship

$$D_1(\text{Pt}-\text{CH}_3) - D_1(\text{Pt}-\text{I}) = +6 \pm 5 \text{ kJ mol}^{-1}$$

which indicates that the platinum-methyl and platinum-iodine bond dissociation energies are virtually the same.

Experimental

$\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)(\text{s})$ was prepared by the method of Cook and Jauhal [7]; m.p. $122-125^\circ\text{C}$ (dec.) (Anal.: Found: C, 60.28; H, 4.76. calcd. for $\text{C}_{38}\text{H}_{34}\text{P}_2\text{Pt}$: C, 61.04; H, 4.58%). cis- and $\text{trans-Pt}(\text{PPh}_3)_2\text{I}_2(\text{s})$, and $\text{cis-Pt}(\text{PPh}_3)_2(\text{CH}_3)\text{I}(\text{s})$ were recovered from the calorimeter vessel, characterised by their infrared spectra [8], and gave satisfactory microanalyses. 1,2-Dichloroethane was dried over magnesium sulphate, purged with nitrogen and distilled, b.p. $82.16-82.23^\circ\text{C}/748.25 \text{ Torr}$. Enthalpies of reaction were measured by use of the LKB 8700 calorimeter, equipped with a 25 ml reaction vessel.

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