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Preliminary communication

ENTHALPY CHANGES IN OXIDATIVE ADDITION REACTIONS OF IODO COMPOUNDS WITH *trans*-$[IrCl(CO)(PMe_3)_2]$ AND DETERMINATION OF A RELATIVE SCALE OF IRIDIUM—LIGAND BOND ENERGIES

G. YONEDA and D.M. BLAKE

Department of Chemistry, The University of Texas at Arlington, Arlington, Texas 76019 (U.S.A.)

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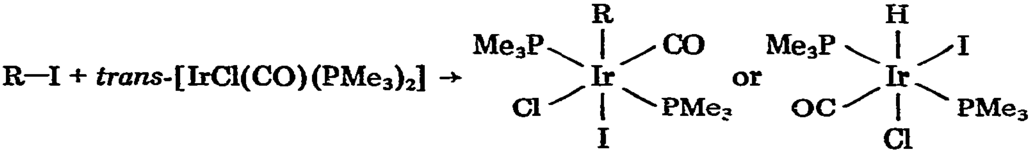
Summary

Enthalpy changes of oxidative addition of a series of eight iodo compounds to *trans*-$[IrCl(CO)(PMe_3)_2]$ have been measured in 1,2-$C_2H_4Cl_2$ solution and the data used in conjunction with other thermochemical data to calculate ΔH° and a relative scale of D (Ir—R) values.

We wish to report the results of our calorimetric study of the addition of organic halides to *trans*-$[IrCl(CO)(PMe_3)_2]$ and their use in derivation of Ir—R bond energy data. The oxidative addition reaction of organic halides with low-valent metal complexes has been very important in the development of organometallic chemistry since it is widely encountered in the synthesis of carbon—metal bonds and is the principle reaction by which organic halides are introduced into stoichiometric or catalytic transition metal mediated syntheses [1—5]. The mechanism for oxidative addition of halo-organic compounds has been elucidated by a number of kinetic [6—9], synthetic and structural studies [1—5]. In contrast, little thermodynamic information for this important type of reaction is available. We have discussed available thermochemical information for reactions of iridium(I) and rhodium(I) complexes in a recent paper reporting application of titration calorimetry to the thermochemical study of this reaction type [10]. To our knowledge, the only thermochemical study to date of the oxidative addition of an organic halide is the recent report by Mortimer, Wilkinson and Puddephatt [11] concerning the addition of methyl iodide to the zerovalent platinum complex $Pt(PPh_3)_2(C_2H_4)$.

The reaction system studied is represented by eq. 1 (R = I, H, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, $C_6H_5CH_2$ or $CH_3C(O)$).



$$R{-}I + trans\text{-}[IrCl(CO)(PMe_3)_2] \rightarrow \begin{array}{ccc} & R & \\ Me_3P & | & CO \\ & Ir & \\ Cl & | & PMe_3 \\ & I & \end{array} \text{ or } \begin{array}{ccc} & H & \\ Me_3P & | & I \\ & Ir & \\ OC & | & PMe_3 \\ & Cl & \end{array} \qquad (1)$$

TABLE 1

ENTHALPY CHANGES (kcal/mol) FOR THE OXIDATIVE ADDITION REACTION OF IODO COMPOUNDS WITH *trans*-[IrCl(CO)(PMe$_3$)$_2$] IN 1,2-$C_2H_4Cl_2$ SOLUTION (ΔH) AND IN THE STANDARD STATE (ΔH°) AND RELATIVE Ir—R BOND DISSOCIATION ENERGIES

Iodo compound	$-\Delta H$ in 1,2-$C_2H_4Cl_2$	$-\Delta H^\circ$	$D(\text{Ir—R}) - D_1(\text{Ir—I})$
I_2	44.3 ± 1.7	39.2 ± 1.9	
HI	38.3 ± 0.7	—	
	40.1 ± 0.7[a]	45[b]	14 ± 3
CH_3I	28.0 ± 1.6	28.1 ± 1.9	0.4 ± 3.2
C_2H_5I	26.2 ± 0.7	25.6 ± 1.2	−3.8 ± 2.8
n-C_3H_7I	24.6 ± 0.9	24.4 ± 1.4	−3.4 ± 3.1
i-C_3H_7I	21.1 ± 2.3	21.1 ± 2.3	−7.4 ± 3.7
$C_6H_5CH_2I$	22.7 ± 1.6	22.7 ± 1.6	−16.6 ± 3.6
$CH_3C(O)I$	30.0 ± 1.0	30.0 ± 1.0	−0.8 ± 3.6

[a] In C_5H_6. [b] Using the mean of the heat of solution of HCl and HBr in C_6H_6 to approximate the heat of solution of HI (−5 kcal/mol).

The stereochemistry of the oxidative addition reactions of the PMe$_3$ complex have been found to follow the familiar pattern of *trans*-addition for organic halides [8,9,12] and *cis*-addition for HI [13]. The products of reaction 1 have been characterized by ^{1}H NMR, and IR spectroscopy and our results are in agreement with those of Labinger [9] and Bennett [14], who have previously characterized many of these or similar compounds.

Titration calorimetric methods previously described [10] were used to measure the enthalpy change for addition of aliquots of the iridium(I) complex to 0.1—0.5 *M* solutions of the iodo compounds in 1,2-dichloroethane. Equilibrium constants are large ($K > 10^4$) so ΔH values were calculated directly from the thermograms. The values reported for ΔH in Table 1 are the average of between 6 and 20 determinations on at least two independently prepared samples of complex and iodo compound. The heats of solution of reactants and products in 1,2-$C_2H_4Cl_2$ have been obtained in the case of R = I, CH_3, C_2H_5, n-C_3H_7 or $CH_3C(O)$. Heats of solution of the iridium(I or III) complexes are in the range +4±1 kcal/mol and for the organic iodides the values are in the range 0.05—0.4 kcal/mol. The heats of solution for I_2 is 5.33±0.13 kcal/mol [11]. For HI no heat of solution data are available so we have approximated it for benzene solution as the mean of the HCl (−5.7 kcal/mol) and HBr (−4.2 kcal/mol) values [15]. From the heats of oxidative addition measured in solution, ΔH, and the data for heats of solution of reactants and products the standard enthalpy changes (all substances in their standard states), ΔH°_{RI}, were calculated (see Table 1). In general for the organic iodides the heat of solution contributions were negligible compared to the experimental errors in ΔH, hence $\Delta H^\circ_{RI} \sim \Delta H$.

A goal of our work has been to obtain information about iridium—ligand bond dissociation energies. Expressing these in terms of the ΔH°_{RI} values we have just discussed, gives eq. 2. In this equation $\Delta H_{\text{sub,Ir·RI}}$ and $\Delta H_{\text{sub,Ir}}$ are the heats of sublimation of IrCl(CO)(PMe$_3$)$_2$·RI and IrCl(CO)(PMe$_3$)$_2$, respectively, and $D(\text{Ir—R})$ is the dissociation energy for R—IrClI(CO)(PMe$_3$)$_2$ and $D(\text{Ir—I})$ is that for I—IrCl(CO)(PMe$_3$)$_2$.

$$D(\text{Ir—R}) + D(\text{Ir—I}) = -\Delta H^\circ_{RI} + D(\text{R—I}) - \Delta H_{\text{sub,Ir·RI}} + \Delta H_{\text{sub,Ir}} + \Delta H_{\text{vap,RI}} \quad (2)$$

The two iridium bond energy terms cannot be determined independently so we have adopted the approach previously used by Mortimer et al. [11] in their work on the thermochemistry of CH_3I addition to platinum(0) compounds. An expression for the difference, $D(\text{Ir—R}) - D(\text{Ir—I})$, is obtained by subtracting data for the I_2 reaction from that for the RI reaction (eq. 3):

$$D(\text{Ir—R}) - D(\text{Ir—I}) = \Delta H^\circ_{I_2} - \Delta H^\circ_{RI} + D(\text{R—I})\ [16] - D(\text{I—I})\ [17] + \Delta H_{\text{vap,RI}}\ [18] - \Delta H_{\text{sub},I_2}\ [17] + \Delta H_{\text{sub,Ir}\cdot I_2} - \Delta H_{\text{sub,Ir}\cdot\text{RI}} \qquad (3)$$

The first two terms are available from our work and the next four are available in the literature. At present data is not available for heats of sublimation of any tertiary phosphine complexes of iridium. Others studying the thermochemistry of iridium and platinum complexes have made the assumption that the difference between the heats of sublimation of the metal complexes is approximately zero [11,19,20].

Making the same assumption allows the set of $D(\text{Ir—R}) - D(\text{Ir—I})$ values in Table 1 to be calculated. These indicate that within the limits of the approximation the trend in $D(\text{Ir—R})$ is $H > CH_3 \sim I \sim CH_3C(O) > n\text{-}C_3H_7 > C_2H_5 > i\text{-}C_3H_7 > C_6H_5CH_2$. The Ir—H bond is significantly stronger than the Ir—C or Ir—I bonds and the Ir—$CH_2C_6H_5$ bond is significantly weaker than the other Ir—C bonds. Interestingly, the trend in $D(\text{Ir—R})$ for the alkyl groups is the same that is found for $D(\text{R—H})$ and $D(\text{R—HgCl})$ [22].

Work is in progress on the determination of heats of sublimation of representative iridium complexes and on determining the factors which influence the heats of oxidative addition reactions.

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