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Thermochemical Studies on Platinum-Olefin Complexes. I

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Using a twin-type calorimeter, the enthalpy changes of solutions and reactions with aqueous KCN solution of Zeise's salts, K[PtCl$_3$(olefin)], were measured. As ligand olefins, ethylene, propylene, 1-butene, 1-pentene, and 1-hexene were employed. It was estimated from a thermochemical analysis that the order of strength of platinum-olefin bonding is as follows; $K[PtCl_3(C_3H_6)] \gtrsim K[PtCl_3(C_2H_4)] \gtrsim K[PtCl_3(1\text{-}C_6H_{12})] \gtrsim K[PtCl_3(1\text{-}C_4H_8)] \gtrsim K[PtCl_3(1\text{-}C_5H_{10})]$. This order was compared with the data of infrared spectra and both the results coincide with each other.

In 1953, the nature of the bonding between an olefinic ligand and platinum atom in Zeise's salt, K[PtCl$_3$(olefin)], was first interpreted by Chatt and Duncanson,[1] by applying the model for the bonding between Ag(I) and olefin ligands proposed by Dewar.[2] According to their model, besides a molecular μ-bond formed between the filled olefin π-molecular orbital and one of the vacant 5d6s6p^2 platinum hybrid orbitals, the overlap between the vacant olefinic antibonding π^*-molecular orbital and one of the filled 5d6s platinum hybrid atomic orbitals was considered as an addition bonding to account for the stability of these metal-olefin complexes. Since then, theoretical and experimental studies on this metal-olefin bonding have been made through measurements of IR,[3] UV,[4] and NMR.[5] In order to get a further information, it would be useful to measure the enthalpy changes of the reactions (1) and (2).

$$K_2PtCl_4(c) + \text{olefin}(g) \longrightarrow K[PtCl_3(\text{olefin})](c) + KCl(c) \qquad (1)$$

$$[PtCl_4]^{2-}(s) + \text{olefin}(g) \longrightarrow [PtCl_3(\text{olefin})]^-(s) + Cl^-(s) \qquad (2)$$

Notations (c), (s), and (g) refer to crystalline, solvated and gaseous state, respectively. The calorimetric measurements of heats of reactions (1) and (2) with water-soluble olefins such as $CH_2{=}CH(CH_2)_nNH_3^+$ were carried out by Denning *et al.*[6] and Orchin,[7] but no measurement was yet done on Zeise's salts having *simple olefins such as ethylene and propylene as ligands. The aim of this paper is to present the result of this* measurement.

Experimental

Synthesis of K[PtCl$_3$(olefin)]. K[PtCl$_3$(C$_2$H$_4$)], K[PtCl$_3$(C$_3$H$_6$)], and K[PtCl$_3$(1-C$_4$H$_8$)] were prepared from K$_2$PtCl$_4$ according to the method described by MacNevin *et al.*[8] The products were recrystallized twice from an aqueous 3% HCl solutions and the purity was checked by elemental analysis. K[PtCl$_3$(1-C$_5$H$_{10}$)] and K[PtCl$_3$(1-C$_6$H$_{12}$)] were prepared as follows; 5 g of K$_2$PtCl$_4$ was dissolved in 50 ml of an aqueous 3% HCl solution and stirred with introducing 1-pentene or 1-hexene for a few weeks in a sealed flask. After filtering, the filtrate was concentrated under low pressure and cooled to get yellow crystals. The crystals were washed with cold water and recrystallized twice from an aqueous 3% HCl solutions and the purity was checked by elemental analyses.

Calorimetric Measurements. A twin-type microcalorimeter, Tokyo Rico Type TCC-65, was used for the following calorimetric measurements. All the measurements were carried out at 25 °C. Anderson reported the next reaction.[9]

$$K[PtCl_3(C_2H_4)](c) + 4KCN(s) \longrightarrow K_2Pt(CN)_4(s) + C_2H_4 + 3KCl(s) \qquad (3)$$

The reaction in an aqueous KCN solution proceeds rapidly and quantitatively at room temperature. The next reaction is also known to proceed in an aqueous KCN solution.

$$K_2PtCl_4(c) + 4KCN(s) \longrightarrow K_2Pt(CN)_4(s) + 4KCl(s) \qquad (4)$$

Here, the following reaction schemes are supposed for convenience of construction of thermodynamic cycles.

$$K_2PtCl_4(c) + 4CN^-(s) \xrightarrow{\Delta H_I} 2K^+(s) + [Pt(CN)_4]^{2-}(s) + 4Cl^-(s) \qquad (I)$$

$$K[PtCl_3(\text{olefin})](c) + 4CN^-(s) \xrightarrow{\Delta H_{II}} K^+(s) + [Pt(CN)_4]^{2-}(s) + 3Cl^-(s) + \text{olefin}(g) \qquad (II)$$

$$K_2PtCl_4(c) \xrightarrow{\Delta H_{III}} 2K^+(s) + [PtCl_4]^{2-}(s) \qquad (III)$$

$$K[PtCl_3(\text{olefin})](c) \xrightarrow{\Delta H_{IV}} K^+(s) + [PtCl_3(\text{olefin})]^-(s) \qquad (IV)$$

$$KCl(c) \xrightarrow{\Delta H_V} K^+(s) + Cl^-(s) \qquad (V)$$

By combining reactions (I), (II), and (V), we got

$$K_2PtCl_4(c) + \text{olefin}(g) \xrightarrow{\Delta H_1} K[PtCl_3(\text{olefin})](c) + KCl(c) \qquad (1)$$

$$\Delta H_1 = \Delta H_I - \Delta H_{II} - \Delta H_V \qquad (5)$$

By combining reactions (I), (II), (III), (IV), and (V), we got

$$[PtCl_4]^{2-}(s) + \text{olefin}(g) \xrightarrow{\Delta H_2} [PtCl_3(\text{olefin})]^-(s) + Cl^-(s) \qquad (2)$$

$$\Delta H_2 = \Delta H_I - \Delta H_{II} - \Delta H_{III} + \Delta H_{IV} \qquad (6)$$

The heats of Reactions (1) and (2) can be obtained from (5) and (b) by using measured values for Reactions (I)—(V).

Heats of Solution. The heat of solution of potassium chloride was measured when an accurately weighed sample (about 37.7 mg) of potassium chloride (guaranteed reagent) was dissolved in 50 ml of pure water in the microcalorimeter. The sample was dried beforehand to constant weight by heating under high vacuum. The heat of solution of potassium tetrachloroplatinate was measured when about 49.8mg (1.2×10^{-4} mol) of potassium tetrachloroplatinate was dissolved in 40 ml of an aqueous 3% HCl solution. Potassium tetrachloroplatinate was used after twice recrystallization.

The heats of solution of $K[PtCl_3(\text{olefin})]$ was determined when about 1.2×10^{-4} mol of $K[PtCl_3(\text{olefin})]$ was dissolved in 40 ml of an aqueous 3% HCl solutions in the microcalorimeter.

Heats of Reactions. An aqueous KCN solution used hereafter was prepared by dissolving about 800 mg of KCN (guaranteed reagent) into 40 ml of pure water. The heat of reaction between potassium tetrachloroplatinate and the aqueous KCN solution was measured when about 200 mg (4.8×10^{-4} mol) of K_2PtCl_4 was put into the KCN solution and reacted. The heats of reaction between $K[PtCl_3(\text{olefin})]$ and the aqueous KCN solution was measured when about 4.8×10^{-4} mol of $K[PtCl_3(\text{olefin})]$ was put into the KCN solutions and reacted in the microcalorimeter.

Results and Discussion

The enthalpy change of potassium chloride at 25 °C was measured thirty times, and the average $\Delta \bar{H}_V$ and the dispersion σ^2 of measured values ΔH_V were determined as follows.

$$\Delta \bar{H}_V = 4.490\ \text{kcal} \cdot \text{mol}^{-1}$$

$$\sigma^2 = 1/(30-1)\sum(\Delta H_V - \Delta \bar{H}_V)^2 = 0.07748$$

We adopted this σ^2 value as a mother dispersion of heat measurements. On the other hand, as the standard value of the heat of solution of potassium chloride at 25 °C was reported to be 4.146 kcal·mol^{-1}, we corrected the measured values by using this standard value.$^{10)}$

The corrected values of the enthalpy changes of solutions of complexes are shown in Table 1 and the enthalpy changes of complexes with an aqueous KCN solution were given in Table 2. The enthalpy changes of reactions (1) and (2) were calculated by using Eqs. (5) and (6) from these values and listed in Table 3.

Let's consider the following thermodynamic cycles to get an information for the bond strength of Pt-olefin in gaseous state.

Table 1. Enthalpy changes of solution of complexes

Molecular formula of complexes	Enthalpy changes of solution ΔH_{III} or ΔH_{IV} (kcal·mol^{-1})
K_2PtCl_4	12.6±0.2
$K[PtCl_3(C_2H_4)]$	10.2±0.2
$K[PtCl_3(C_3H_6)]$	10.5±0.2
$K[PtCl_3(1\text{-}C_4H_8)]$	10.4±0.2
$K[PtCl_3(1\text{-}C_5H_{10})]$	10.9±0.2
$K[PtCl_3(1\text{-}C_6H_{12})]$	10.8±0.2

Table 2. Enthalpy changes of reactions of complexes with aqueous KCN solution

Molecular formula of complexes	Enthalpy changes of reactions ΔH_I or ΔH_{II} (kcal·mol^{-1})
K_2PtCl_4	−87.8±0.3
$K[PtCl_3(C_2H_4)]$	−79.3±0.4
$K[PtCl_3(C_3H_6)]$	−77.0±0.6
$K[PtCl_3(1\text{-}C_4H_8)]$	−80.7±0.4
$K[PtCl_3(1\text{-}C_5H_{10})]$	−79.2±0.4
$K[PtCl_3(1\text{-}C_6H_{12})]$	−80.8±0.5

Table 3. Enthalpy changes of Reactions (1) and (2)

Olefin	ΔH_1 (kcal·mol^{-1})	ΔH_2 (kcal·mol^{-1})
Ethylene	−12.6±0.5	−10.9±0.6
Propylene	−14.9±0.7	−13.2±0.7
1-Butene	−11.3±0.5	−9.3±0.6
1-Pentene	−12.7±0.5	−10.2±0.6
1-Hexene	−11.1±0.7	−8.8±0.7

$$\begin{tikzcd}
K_2PtCl_4(c) + \text{olefin}(g) \arrow[rr, "\Delta H_1"] & & K[PtCl_3(\text{olefin})](c) + KCl(c) \\
K_2PtCl_4(g) + \text{olefin}(g) \arrow[u, "\Delta H_{c1}"] \arrow[r, "\Delta H_d"] \arrow[d, "\Delta H_{s1}"] & KPtCl_3(g) + KCl(g) + \text{olefin}(g) \arrow[r, "\Delta H"] & K[PtCl_3(\text{olefin})](g) + KCl(g) \arrow[u, shift right, "\Delta H_{c2}"'] \arrow[u, shift left, "\Delta H_{c3}"] \arrow[d, shift right, "\Delta H_{s2}"'] \arrow[d, shift left, "\Delta H_{s3}"] \\
{[PtCl_4]^{2-}(s) + 2K^+(s) + \text{olefin}(g)} \arrow[rr, "\Delta H_2"] & & {[PtCl_3(\text{olefin})]^-(s) + 2K^+(s) + Cl^-(s)}
\end{tikzcd}$$

$$\begin{aligned}\Delta H &= \Delta H_1 + \Delta H_{c1} - \Delta H_{c2} - \Delta H_{c3} - \Delta H_d \\ &= \Delta H_2 + \Delta H_{s1} - \Delta H_{s2} - \Delta H_{s3} - \Delta H_d \qquad (7)\end{aligned}$$

Here, ΔH_{c1}, ΔH_{c2}, and ΔH_{c3} are enthalpy changes of crystallization, and ΔH_{s1}, ΔH_{s2}, and ΔH_{s3} are enthalpy changes of electrolytic dissolution of K_2PtCl_4, KCl, and $K[PtCl_3(\text{olefin})]$, respectively. ΔH_{c1}, ΔH_{c3}, ΔH_{s1}, ΔH_{s3} and ΔH_d are independent of olefin. By collecting these olefin-independent terms, Eq. (7) is rearranged as follows.

$$\begin{aligned}\Delta H &= \Delta H_1 - \Delta H_{c2} + \Delta H' \\ &= \Delta H_2 - \Delta H_{s2} + \Delta H''\end{aligned}$$

where

$$\Delta H' = \Delta H_{c1} - \Delta H_{c3} - \Delta H_d$$

$$\Delta H'' = \Delta H_{s1} - \Delta H_{s3} - \Delta H_d$$

The value of ΔH_{c2} is the lattice energy of $K[PtCl_3(\text{olefin})]$ and the value of ΔH_{s2} contains the dissociation energy of $K[PtCl_3(\text{olefin})]$ and the solvating energies of resulting ions, K^+ and $[PtCl_3(\text{olefin})]^-$. It would be tentatively assumed that these values are not influenced by the kind of olefin to a greater extent. Under this assumption, we get the following strength order of platinum-olefin bonds.

$$K[PtCl_3(C_3H_6)] \gtrsim K[PtCl_3(C_2H_4)] \gtrsim K[PtCl_3(1\text{-}C_6H_{12})]$$
$$\gtrsim K[PtCl_3(1\text{-}C_4H_8)] \gtrsim K[PtCl_3(1\text{-}C_5H_{10})]$$

We may compare this result with that of infrared spectrum. Sorzano$^{11)}$ reported that the band of 491 cm^{-1} in $K[PtCl_3(C_2H_4)]$ is assigned to the Pt-|| stretching vibration. Some authors$^{3,12)}$ assigned the 1526 cm^{-1} band to the C=C stretching vibration. Recently, Hiraishi$^{13)}$ assigned the 1250 cm^{-1} band to this mode by considering the Raman spectrum, and assigned the 1526 cm^{-1} band to the C–H scissoring vibration. The values of the infrared spectra of various complexes measured in the present investigation are listed in Table 4. It is seen from this table that the frequency of Pt-|| stretching vibration in the propylene complex is higher than that in the other complexes. The higher the frequency of Pt-|| stretching vibration is,

Table 4. Infrared data of $K[PtCl_3(olefin)]$

Molecular formula	Pt-‖ stretching vib. cm^{-1}	C=C stretching vib. cm^{-1}	
$K[PtCl_3(C_2H_4)]$	490	1250	1526
$K[PtCl_3(C_3H_6)]$	495	1245	1506
$K[PtCl_3(1\text{-}C_4H_8)]$	490	1250	1504
$K[PtCl_3(1\text{-}C_5H_{10})]$	492	1252	1501
$K[PtCl_3(1\text{-}C_6H_{12})]$	490	1251	1500

the stronger the bonding is and, therefore, the bonding between platinum-propylene is considered to be stronger than the others. Moreover, it is known that the C=C stretching vibration shifts to lower frequencies upon coordination to the Pt atom. According to Hiraishi, the C=C stretching vibration is in a region near 1250 cm^{-1}. This band is 1250 cm^{-1} in the case of the ethylene complex and 1245 cm^{-1} in the case of the propylene complex. These values mean that propylene coordinates to the Pt atom stronger than ethylene. These results coincide with our data of calorimetric measurements.

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