

# Thermochemical Studies on Platinum-Olefin Complexes. I

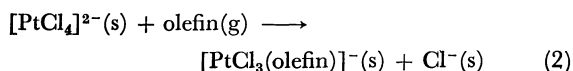
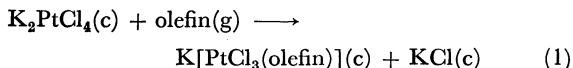
Manabu SENŌ, Kazutoshi IWAMOTO, and Teruzo ASAHARA

*Institute of Industrial Science, The University of Tokyo, Minato-ku, Tokyo 106*

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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;  $K[PtCl_3(C_3H_6)] \gtrsim K[PtCl_3(C_2H_4)] \gtrsim K[PtCl_3(1-C_6H_{12})] \gtrsim K[PtCl_3(1-C_4H_8)] \gtrsim K[PtCl_3(1-C_5H_{10})]$ . 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,<sup>1)</sup> by applying the model for the bonding between  $Ag(I)$  and olefin ligands proposed by Dewar.<sup>2)</sup> According to their model, besides a molecular  $\mu$ -bond formed between the filled olefin  $\pi$ -molecular orbital and one of the vacant  $5d_{6s}6p^2$  platinum hybrid orbitals, the overlap between the vacant olefinic antibonding  $\pi^*$ -molecular orbital and one of the filled  $5d_{6s}$  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,<sup>3)</sup> UV,<sup>4)</sup> and NMR.<sup>5)</sup> In order to get a further information, it would be useful to measure the enthalpy changes of the reactions (1) and (2).



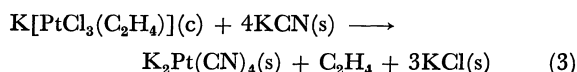
Notations (c), (s), and (g) refer to crystalline, solvated and gaseous state, respectively. The calorimetric measurements of heats of reactions (1) and (2) with water-soluble olefins such as  $CH_2=CH(CH_2)_nNH_3^+$  were carried out by Denning *et al.*<sup>6)</sup> and Orchin,<sup>7)</sup> but no measurement 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

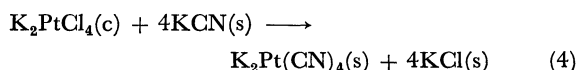
**Synthesis of  $K[PtCl_3(olefin)]$ .**  $K[PtCl_3(C_2H_4)]$ ,  $K[PtCl_3(C_3H_6)]$ , and  $K[PtCl_3(1-C_4H_8)]$  were prepared from  $K_2PtCl_4$  according to the method described by MacNevin *et al.*<sup>8)</sup> The products were recrystallized twice from an aqueous 3% HCl solutions and the purity was checked by elemental analysis.  $K[PtCl_3(1-C_5H_{10})]$  and  $K[PtCl_3(1-C_6H_{12})]$  were prepared as follows; 5 g of  $K_2PtCl_4$  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

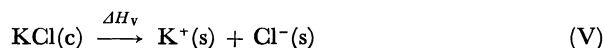
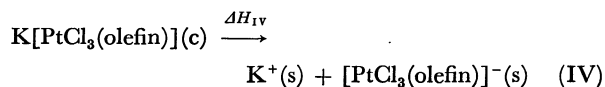
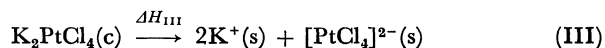
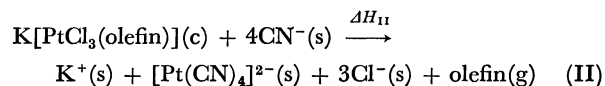
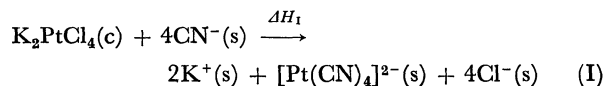
calorimetric measurements. All the measurements were carried out at 25 °C. Anderson reported the next reaction.<sup>9)</sup>



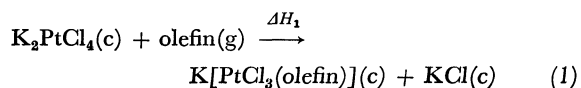
The reaction in an aqueous KCN solution proceeds rapidly and quantitatively at room temperature. The next reaction is also known to proceed in an aqueous KCN solution.



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

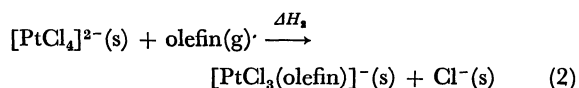


By combining reactions (I), (II), and (V), we got



$$\Delta H_I = \Delta H_{II} - \Delta H_{III} - \Delta H_V \quad (5)$$

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



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

The heats of Reactions (1) and (2) can be obtained from (5) and (6) 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 49.8 mg ( $1.2 \times 10^{-4}$  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  $K[PtCl_3(olefin)]$  was determined when about  $1.2 \times 10^{-4}$  mol of  $K[PtCl_3(olefin)]$  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 ( $4.8 \times 10^{-4}$  mol) of  $K_2PtCl_4$  was put into the KCN solution and reacted. The heats of reaction between  $K[PtCl_3(olefin)]$  and the aqueous KCN solution was measured when about  $4.8 \times 10^{-4}$  mol of  $K[PtCl_3(olefin)]$  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  $\sigma^2$  of measured values  $\Delta H_v$  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  $\sigma^2$  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  $4.146 \text{ kcal} \cdot \text{mol}^{-1}$ , we corrected the measured values by using this standard value.<sup>10)</sup>

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

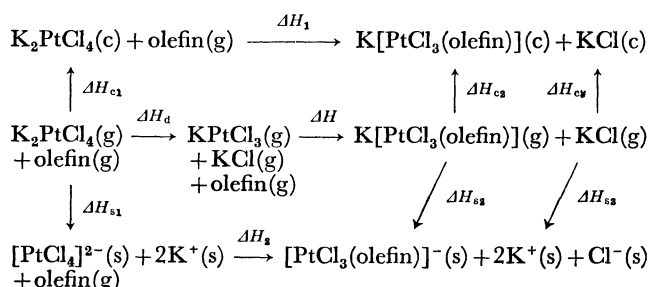
Molecular formula of complexes	Enthalpy changes of solution $\Delta H_{III}$ or $\Delta H_{IV}$ ( $\text{kcal} \cdot \text{mol}^{-1}$ )
$K_2PtCl_4$	$12.6 \pm 0.2$
$K[PtCl_3(C_2H_4)]$	$10.2 \pm 0.2$
$K[PtCl_3(C_3H_6)]$	$10.5 \pm 0.2$
$K[PtCl_3(1-C_4H_8)]$	$10.4 \pm 0.2$
$K[PtCl_3(1-C_5H_{10})]$	$10.9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

TABLE 2. ENTHALPY CHANGES OF REACTIONS OF COMPLEXES WITH AQUEOUS KCN SOLUTION

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

TABLE 3. ENTHALPY CHANGES OF REACTIONS (1) AND (2)

Olefin	$\Delta H_1$ ( $\text{kcal} \cdot \text{mol}^{-1}$ )	$\Delta H_2$ ( $\text{kcal} \cdot \text{mol}^{-1}$ )
Ethylene	$-12.6 \pm 0.5$	$-10.9 \pm 0.6$
Propylene	$-14.9 \pm 0.7$	$-13.2 \pm 0.7$
1-Butene	$-11.3 \pm 0.5$	$-9.3 \pm 0.6$
1-Pentene	$-12.7 \pm 0.5$	$-10.2 \pm 0.6$
1-Hexene	$-11.1 \pm 0.7$	$-8.8 \pm 0.7$



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

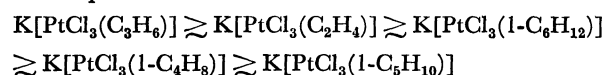
Here,  $\Delta H_{c1}$ ,  $\Delta H_{c2}$ , and  $\Delta H_{c3}$  are enthalpy changes of crystallization, and  $\Delta H_{s1}$ ,  $\Delta H_{s2}$ , and  $\Delta H_{s3}$  are enthalpy changes of electrolytic dissolution of  $K_2PtCl_4$ ,  $KCl$ , and  $K[PtCl_3(olefin)]$ , respectively.  $\Delta H_{c1}$ ,  $\Delta H_{c3}$ ,  $\Delta H_{s1}$ ,  $\Delta H_{s3}$  and  $\Delta H_d$  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

$$\begin{aligned}
 \Delta H' &= \Delta H_{c1} - \Delta H_{c3} - \Delta H_d \\
 \Delta H'' &= \Delta H_{s1} - \Delta H_{s3} - \Delta H_d
 \end{aligned}$$

The value of  $\Delta H_{c2}$  is the lattice energy of  $K[PtCl_3(olefin)]$  and the value of  $\Delta H_{s2}$  contains the dissociation energy of  $K[PtCl_3(olefin)]$  and the solvating energies of resulting ions,  $K^+$  and  $[PtCl_3(olefin)]^-$ . 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.



We may compare this result with that of infrared spectrum. Sorzano<sup>11)</sup> reported that the band of  $491 \text{ cm}^{-1}$  in  $K[PtCl_3(C_2H_4)]$  is assigned to the Pt-|| stretching vibration. Some authors<sup>3,12)</sup> assigned the  $1526 \text{ cm}^{-1}$  band to the C=C stretching vibration. Recently, Hiraishi<sup>13)</sup> assigned the  $1250 \text{ cm}^{-1}$  band to this mode by considering the Raman spectrum, and assigned the  $1526 \text{ cm}^{-1}$  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
$K[PtCl_3(1-C_4H_8)]$	490	1250 1504
$K[PtCl_3(1-C_5H_{10})]$	492	1252 1501
$K[PtCl_3(1-C_6H_{12})]$	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.

## References

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