Kinetic Parameters of Thermal Dehydration and Decomposition of Zeise's Salt Hydrates

Manabu Senō, Kazutoshi Iwamoto, and Teruzo Asahara
Institute of Industrial Science, University of Tokyo, Roppongi, Minato-ku, Tokyo 106

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The kinetic parameters of the dehydration of Zeise's salt hydrates, $K[PtCl_3(olefin)]\cdot H_2O$, (olefin; $CH_2{=}CH_2$, $CH_3CH{=}CH_2$, $C_2H_5CH{=}CH_2$, $n\text{-}C_3H_7CH{=}CH_2$ and $n\text{-}C_4H_9CH{=}CH_2$) and the thermal decomposition of Zeise's dimers were determined by using DTA and TG. By comparing the kinetic parameters with the data of IR and the enthalpy change of dehydration, it was shown that the important factor in determining the kinetic behavior of the dehydration is an extent of deformation of lattice at the transition state. Similarly, it was suggested that the bulkiness of ligand olefin is an important factor in governing the kinetics of the thermal decomposition reactions.

In a previous paper,[1)] it was shown from the investigation of the dehydration reaction of Zeise's salt that the dehydrated Zeise's salt contains some amount of the dimer. The content of the dimer was determined and the thermochemical properties of thermal decomposition reactions were examined. In the present paper, the kinetic parameters of the dehydration process of Zeise's salt and the thermal decomposition process of Zeise's dimer were determined from the data of differential thermal analysis (DTA) and thermogravimetry (TG). The activation energy and the activation entropy of dehydration process of Zeise's salts decrease remarkably as the ligand olefin becomes smaller. On the other hand, the decreasing order of the activation energy of the thermal decomposition process of Zeise's dimers is as follows;

$$[PtCl_2(n\text{-}C_4H_9CH{=}CH_2)]_2 > [PtCl_2(n\text{-}C_3H_7CH{=}CH_2)]_2 >$$
$$[PtCl_2(C_2H_5CH{=}CH_2)]_2 \approx [PtCl_2(CH_2{=}CH_2)] >$$
$$[PtCl_2(CH_3CH{=}CH_2)]_2$$

Experimental

Syntheses of Zeise's Salts K[PtCl$_3$(olefin)]. Zeise's salt hydrates $K[PtCl_3(olefin)]\cdot H_2O$ were prepared from K_2PtCl_4 and olefins according to the method described by MacNevin *et al.*[2)] The products were recrystallized twice from 3% aqueous HCl solutions and dehydrated by storing in a $CaCl_2$ desiccator in 2—3 weeks. The purities were checked by elementary analyses.

Syntheses of Zeise's Dimers [PtCl$_2$(olefin)]$_2$. Dimers of Zeise's salts $[PtCl_2(olefin)]_2$ were prepared from Zeise's salts according to the method described by Moeller.[3)] The products were confirmed by elementary analyses.

Measurements of Decomposition Processes. A thermal analyzer DT-20B (Shimadzu) and a thermo flex (Rigaku Denki) were used for characterization of thermal decomposition processes. Most of the measurements were carried out at the increasing rate of temperature of 1.25 °C/min under N_2 flow. The data of DTA, from which the kinetic parameters of the dehydration process were determined, were measured at the increasing rates of temperature of 5 °C/min, 10 °C/min, 20 °C/min and 40 °C/min, respectively.

Results and Discussion

Zeise's salt has one mole of crystalline water. The absorption peaks of the infrared spectra ascribed to the crystalline water in the complexes with various olefins are shown in Table 1. Asymmetric and symmetric stretching vibrations of the O–H band shift to a lower frequency side and the bending vibration shifts to a higher frequency side compared with those of a free water molecule, but these shifts are not so large as those in liquid water as being seen in Table 1. This means that the water molecule in Zeise's salt interacts with chlorine atoms to form partially hydrogen bonds. As a ligand olefin becomes large, the asymmetric stretching vibration shifts somewhat to a higher frequency. The other vibrations do not change so clearly as asymmetric stretching vibration.

Table 1. IR spectra of crystalline water of Zeise's salt hydrate, $K[PtCl_3(olefin)]\cdot H_2O$

Complexes	Asym. stretch. vib. (cm^{-1})	Sym. strech. vib. (cm^{-1})	Bending vib. (cm^{-1})
$K[PtCl_3(C_2H_4)]\cdot H_2O$	3540	3480	1614
$K[PtCl_3(C_3H_6)]\cdot H_2O$	3540	3480	1618
$K[PtCl_3(\Delta'\text{-}C_4H_8)]\cdot H_2O$	3550	3500	1620
$K[PtCl_3(\Delta'\text{-}C_5H_{10})]\cdot H_2O$	3555	3500	1618
$K[PtCl_3(\Delta'\text{-}C_6H_{12})]\cdot H_2O$	3565	3500	1618
Free H_2O	3755.8	3654.5	1595.0[9)]
Liquid H_2O	3430	3210	1650[9)]

These observations are consistent with the results of X-ray analysis.[4,5)] According to Black *et al.*,[5)] $K[PtCl_3(CH_2{=}CH_2)]\cdot H_2O$ forms a monoclinic crystal, $a{=}10.750$ Å $b{=}8.405$ Å, $c{=}4.836$ Å, $\beta{=}97.73°$. There are a chain of alternate potassium ions and triangles of chlorine atoms and a chain of hydrogen bonds $\cdots Cl^- \cdots H\text{–}O\text{–}H \cdots$ parallel to the c axis and these two chains are cross-linked by the coordinate bonds within the complex ions and by the ionic interactions in chains of $\text{–}O\text{–}K^+\text{–}$ which are parallel to the b axis.

The dehydration reaction of Zeise's salt hydrates was analyzed by using DTA. Zeise's salt hydrates lose one mole of crystalline water by heating at about 60—80 °C. The activation energy and the order of dehydration reaction were estimated by using the method of Kissinger.[6)] The following equations serve as a basis of analysis of DTA curve.

$$\ln \frac{\phi}{T_m^2} = \ln A - \frac{E_a}{RT_m} \qquad (1)$$

$$n = 1.26S^{1/2} \qquad (2)$$

$$S = \frac{(d^2x/dt^2)_1}{(d^2x/dt^2)_2} \qquad (3)$$

Table 2. Activation energies and reaction orders of dehydration of Zeise's salt hydrate, $K[PtCl_3(olefin)]\cdot H_2O$

Complexes	Temp (°C)	n	E_a (kcal·mol^{-1})	ln A	$\Delta S^{\neq}$ (cal·K^{-1})	ΔH (kcal·mol^{-1})
$K[PtCl_3(C_2H_4)]\cdot H_2O$	67	0.72	46.7	70.0	80.7	15.5±0.5
$K[PtCl_3(C_3H_6)]\cdot H_2O$	76	0.90	30.8	44.8	30.6	15.3±0.5
$K[PtCl_3(\Delta'\text{-}C_4H_8)]\cdot H_2O$	73	1.11	26.8	38.4	17.9	16.0±1.0
$K[PtCl_3(\Delta'\text{-}C_5H_{10})]\cdot H_2O$	59	0.89	19.4	28.9	−1.0	13.3±1.0
$K[PtCl_3(\Delta'\text{-}C_6H_{12})]\cdot H_2O$	65	0.82	15.3	22.4	−13.9	14.0±1.0

ΔH is the enthalpy change in dehydration of Zeise's salt hydrate.[1]

In these equations, ϕ is the constant rate of temperature rise, T_m is the temperature giving a maximum rate of dehydration, n is the order of dehydration reaction, E_a is the activation energy, A is the frequency factor, R is the gas constant and S is called as a shape index. The values of T_m were determined at the rates of temperature rise ϕ of 5, 10, 20 and 40 °C/min and therefrom the kinetic parameters were obtained. The results of analyses are shown in Table 2. The activation energy of dehydration of the complexes decreases as the ligand olefin becomes larger. The values of $\Delta S^{\neq}$ are positive and larger for a smaller ligand olefin. The values of activation energy and activation entropy change greatly when the ligand olefin changes. On the other hand, the enthalpy change of dehydration does not change so remarkably as the activation energy and entropy. These results suggest that the bond energy of water in lattice is not an important factor which governs the transition state of dehydration reaction, but the energy required for deformation of lattice structure would be an important factor. During the process of dehydration, the lattice structure would be deformed markedly and the transition state would have a loose deformed structure, which ensures a large activation energy and a positive activation entropy.

For the complex with smaller ligand olefin such as ethylene, the transition state would be so far from the initial state and the deformation at the transition state becomes small as the ligand olefin is larger. This consideration accounts for the result in Table 2.

As being described in the preceding paper,[1] Zeise's salt hydrate loses crystalline water and at the same time rearranges partially into a dimer $[PtCl_2(olefin)]_2$. The above results for activation parameters of dehydration are for the overall reactions at the dehydration temperatures.

When the Zeise's salt is continued to heat after dehydration, it decomposes in two steps. The first step is the thermal decomposition of the dimer formed during the dehydration, as being revealed by the preceding paper.[1] The reaction order and the activation energy of the first step were calculated by using the Freeman-Carroll method.[7] The DTA curves of thermal decomposition of the dimers are too broad and obscure to calculate activation parameters by using the method of Kissinger and, since the decrease in weight is slow and large, the method of Freeman-Carroll is convenient. On the contrary, the dehydration process of Zeise's salt is too fast to measure exactly the weight loss, and the method of Kissinger is more convenient.

It was supposed[1] that the first step reaction proceeds as shown by Eq. 4,

$$[PtCl_2(olefin)]_2 \rightarrow Pt + PtCl_2 + Cl_2 + 2olefin \tag{4}$$

Then, the rate of decomposition reaction is tentatively assumed to be expressed by Eq. 5,

$$-\frac{dX}{dt} = kX^{\alpha} \tag{5}$$

where X is the amount of the reactant $[PtCl_2(olefin)]_2$ in the specimen, k is the rate constant and α is the reaction order with respect to the reactant. Now, the total amount of chemical species in this reaction system varies in progress of decomposition reaction and, therefore, we put

$$X = \frac{n}{N} \tag{6}$$

where n is the amount of the reactant and N is the total amount in molar unit in the reaction mixture at time t. Then,

$$\frac{-(E_a/R)\Delta(1/T)}{\Delta(\ln N - \ln n)} = \alpha + \frac{\Delta \ln(n\cdot dN/dt - N\cdot dn/dt) - 2\Delta \ln N}{\Delta(\ln N - \ln n)} \tag{7}$$

We could obtain the values of α and E_a from the plot $[\Delta\ln(n\cdot dN/dt - N\cdot dn/dt) - 2\Delta\ln N]/\Delta(\ln N - \ln n)$ against $\Delta(1/T)/\Delta(\ln N - \ln n)$ obtained by the thermogravimetric measurement. The results are shown in

Table 3. Activation energies, reaction orders and enthalpy changes of thermal decomposition of Zeise's dimers

Complexes	E_a (kcal mol^{-1})	α	$\Delta H^{8)}$ (kcal mol^{-1})
$[PtCl_2(C_2H_4)]_2$	36	3	15.5±0.5$^{a)}$
$[PtCl_2(C_3H_6)]_2$	30	−0.6	18.1±0.5*
$[PtCl_2(\Delta'\text{-}C_4H_8)]_2$	36	0	12.7±0.5$^{a)}$
$[PtCl_2(\Delta'\text{-}C_5H_{10})]_2$	42	2	7.4±1.0$^{b)}$
$[PtCl_2(\Delta'\text{-}C_6H_{12})]_2$	46	1	6.8±1.0$^{b)}$

a) Total enthalpy change in the two-step thermal decomposition. b) Enthalpy change in the second step of the thermal decomposition.

Table 3. These values would contain rather large errors and the reliability of α is estimated to be about ± 1, and that of activation energy to be about ± 2 kcal mol^{-1}. Except for the ethylene complex, the activation energy increases as the ligand olefin is larger.

There is no relation between the bond strength of π-bond and the activation energy. If the cleavage of π-bond is a rate determining step, the bond strength of π-bond would be closely related to the activation energy. The values of enthalpy change of Eq. 8 are different slightly among the complexes with various olefins.[8)]

$$PtCl_4^{2-} + \text{olefin} \rightarrow [PtCl_3(\text{olefin})]^- + Cl^- \qquad (8)$$

While, there is a fairly large difference between different olefin complexes in the activation energy of thermal decomposition. These results suggest that the bulkiness of ligand olefin would be an important factor in governing kinetics of thermal decomposition of Pt-olefin complexes.

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