

JOM 23686

# Ionic hydrogen bond and deprotonation of cationic hydride $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{OsH}]^+\text{A}^-$

L.M. Epstein, E.S. Shubina, A.N. Krylov, A.Z. Kreindlin and M.I. Rybinskaya

A.N. Nesmeyanov Institute of Organo-Element Compounds of the Russian Academy of Science, Vavilov str., 28, Moscow B-334 (Russian Federation)

(Received February 10, 1993)

## Abstract

Ionic hydrogen bond formation by protonated metallocene and the anion,  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{OsH}]^+ \dots ^-\text{OOCF}_3$ , as the first stage of deprotonation was discovered by IR spectra in low polar solvents. The equilibrium between the molecular and ionic hydrogen-bonded complexes,  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Os} \dots \text{HOOCF}_3$ , formed after proton transfer is investigated. The structure of the ion pairs  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{OsH}]^+\text{A}^-$  ( $\text{A} = \text{BF}_4, \text{PF}_6, \text{CF}_3\text{SO}_3$ ) in the solid state and solution are discussed.

## 1. Introduction

Recently, we reported that cationic hydride  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{OsH}]^+\text{PF}_6^-$  (**1**) can form ion-molecular hydrogen bonds with neutral bases containing phosphoryl groups [1]. In the case of  $(\text{Me}_2\text{N})_3\text{PO}$ , the equilibrium between such hydrogen-bonded complex and the product of deprotonation, **1**, in  $(\text{CH}_2\text{Cl}_2)$  solution was found.

The object of this study was to examine the ability of protonated decamethylzirconocene to form ionic hydrogen-bonded complexes with the different anions  $[\text{Cp}^*_2\text{OsH}]^+\text{A}^-$  ( $\text{A} = \text{PF}_6^-$  (**1**),  $\text{BF}_4^-$  (**2**),  $\text{CF}_3\text{SO}_3^-$  (**3**)). We also elucidated the role of such hydrogen bonds in the proton transfer reaction. The salt  $\text{K}^+\text{CF}_3\text{COO}^-$  (**4**) was chosen for this investigation. This salt can be dissolved in low polar media ( $\text{Cl}_4 + \text{CHCl}_3$ ) in the presence of 18-crown-6. The key advantage of **4** is the known IR spectral characteristics of  $\nu(\text{CO})$  stretching vibrations attributed to the ionic and molecular complexes of  $\text{CF}_3\text{COOH}$  with organic bases ( $1800\text{--}1600\text{ cm}^{-1}$ ) [2].

We now report the results of a study of the IR spectra of the salts **1–3** and the products of their interaction with **4**. The spectra were measured in the solid state and in solution ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CCl}_4 + \text{CHCl}_3$ , 1:1) in the  $\nu(\text{OsH})$  and  $\nu(\text{CO})$  ranges.

Correspondence to: Dr. L.M. Epstein.

## 2. Results and discussion

As can be inferred from Table 1, the changes in the position and the shape of the  $\nu(\text{OsH})$  bands on going from the solid state to solution is dependent on the anions. The weak  $\nu(\text{OsH})$  bands of the solid samples are observed in the range  $2164\text{--}2173\text{ cm}^{-1}$  with a high frequency shoulder,  $2194\text{--}2200\text{ cm}^{-1}$ , for all three salts. The spectra of the solutions are different. In the case of **3** ( $\text{A}^- = \text{CF}_3\text{SO}_3^-$ ), only one high frequency band at  $2195\text{ cm}^{-1}$  is revealed with weak low frequency asymmetry. In the IR spectrum of the salt with  $\text{PF}_6^-$  anion, **1**, the low frequency shoulder remains, as shown previously [1]. For the salt **2** with  $\text{A}^- = \text{BF}_4^-$ , the intensities of two components at  $2194\text{ cm}^{-1}$  and  $2160\text{ cm}^{-1}$  are similar (Fig. 1). The assignment of the low frequency component of this doublet to the stretching vibrations of the OsH groups bonded with anions is supported by the character of the concentration dependence. Figure 2 shows that the intensity of the low frequency shoul-

TABLE 1. IR spectra of  $[\text{Cp}^*_2\text{OsH}]^+ \dots \text{A}^-$  in the region  $\nu[\text{OsH}]^+$  in the solid state and in solution

$\nu[\text{OsH}]^+ (\text{cm}^{-1})$	$\text{PF}_6^-$	$\text{BF}_4^-$	$\text{CF}_3\text{SO}_3^-$
Solid state	2194sh 2164	2195sh 2162	2200sh 2173
In $\text{CH}_2\text{Cl}_2$	2195 2160sh	2192 2166	2195 Low freq. ass

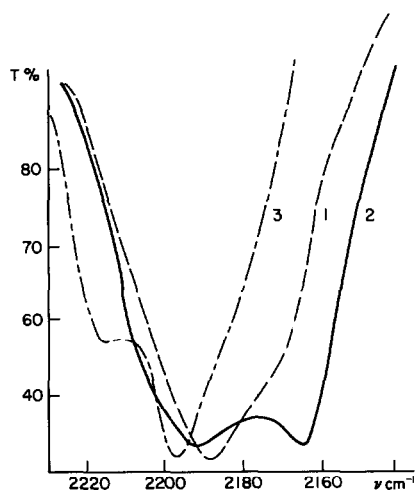


Fig. 1. IR spectra of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{OsH}]^+\text{A}^-$  ( $\nu[\text{OsH}]$  bands)  $\text{A} = \text{PF}_6^-$  (1),  $\text{BF}_4^-$  (2),  $\text{CF}_3\text{SO}_3^-$  (3), in  $\text{CH}_2\text{Cl}_2$  solution ( $c = 0.08$  mol/l,  $d = 1$  mm).

der ( $2160\text{ cm}^{-1}$ ) is lowered with a decrease in the concentration of 1. There is some similarity of these spectral properties to that of the ion molecular hydrogen bond  $[\text{OsH}]^+ \dots \text{OP}$  [1]. Thus, we can assume that these ion pairs are stabilized by ionic hydrogen bonding of the  $[\text{OsH}]^+ \dots \text{A}^-$  type.

The existence of ionic hydrogen-bonded complexes was clearly shown by the interaction of the cationic hydride with trifluoroacetate, which is more capable of hydrogen bonding than the anions discussed above. The broad  $\nu(\text{OsH})$  band of the hydrogen-bonded complex  $[\text{OsH}]^+ \dots \text{OOCF}_3$  (Fig. 3) ( $2180\text{ cm}^{-1}$ ) is observed at low temperature. The intensity of this band decreases with a rise in temperature. Similar changes were observed earlier for ion-molecular complexes of 1

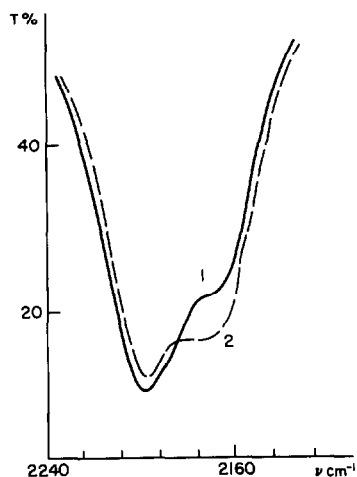


Fig. 2. IR spectra of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{OsH}]^+\text{PF}_6^-$  ( $\nu[\text{OsH}]$  bands) ( $c = 0.08$  mol/l,  $d = 1$  mm (1) and  $c = 0.02$  mol/l,  $d = 4$  mm (2), in  $\text{CH}_2\text{Cl}_2$  solution.

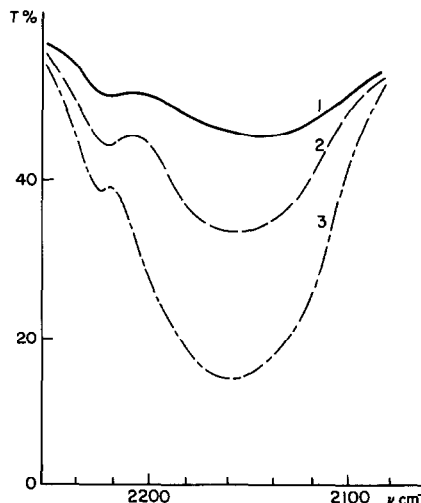
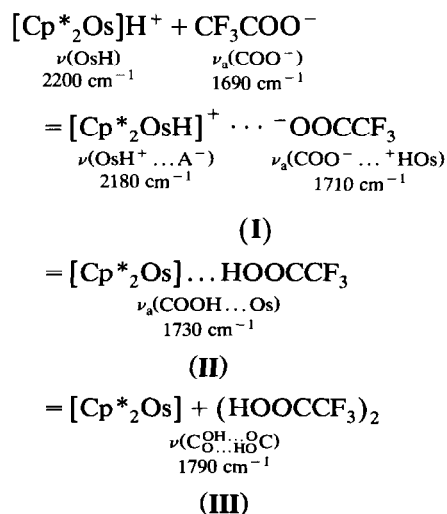


Fig. 3. Temperature dependence of  $\nu[\text{OsH}]$  bands of  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{OsH}]^+\text{PF}_6^-$  (0.08 mol/l) and  $\text{CF}_3\text{COOK}$  (0.1 mol/l), in  $\text{CH}_2\text{Cl}_2$  solution with 18-crown-6 ( $d = 1$  mm).  $t = 20^\circ\text{C}$  (1),  $-20^\circ\text{C}$  (2) and  $-60^\circ\text{C}$  (3).

with  $(\text{Me}_2\text{N})_3\text{PO}$  and were accounted for by proton transfer to this phosphoryl base [1].

A parallel investigation of the temperature dependence in the two regions, *i.e.*  $\nu(\text{OsH})$  and  $\nu(\text{CO})$  ( $1800\text{--}1580\text{ cm}^{-1}$ ), made it possible to fix all the stages of this cationic hydride deprotonation in low polar media.

We found that the ionic hydrogen-bonded complex  $\text{OsH}^+ \dots \text{OOCF}_3$  (I) is in equilibrium with the molecular H-complex, which is formed after proton transfer,  $(\text{Cp}^*_2\text{Os} \dots \text{HOOCF}_3)$  (II). It was also demonstrated that equilibrium exists between II and acid dimers III, appearing due to partial molecular complex dissociation.



The intensity of the band at  $1710\text{ cm}^{-1}$  increases with a decrease in temperature, as well as the band at  $2180\text{ cm}^{-1}$ . Thus, it was assigned to the stretching

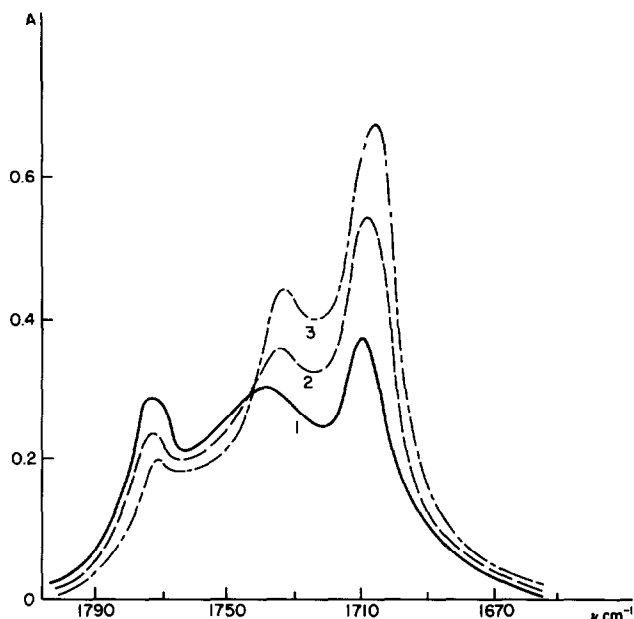


Fig. 4. Temperature dependence of  $\nu[\text{CO}]$  bands of  $\text{CF}_3\text{COOK}$  (0.001 mol/l) and  $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{OsH}]^+\text{PF}_6^-$  (0.08 mol/l), in  $\text{CH}_2\text{Cl}_2$  solution with 18-crown-6 ( $d = 1$  mm).  $t = 20^\circ\text{C}$  (1),  $-20^\circ\text{C}$  (2) and  $-60^\circ\text{C}$  (3).

vibrations of  $\nu_a(\text{COO}^-)$  of ionic hydrogen-bonded complex (I) (Fig. 4). It should be noted that this band is higher than that for the "naked" anion  $\text{CF}_3\text{COO}^-$  ( $1690\text{ cm}^{-1}$ )  $\text{K}^+\text{CF}_3\text{COO}^-$  salt in  $\text{CCl}_4 + \text{CHCl}_3$  in the presence of 18-crown-6. However, the last band is not revealed if protonated osmocene is used in excess (Fig. 4). The band at  $1730\text{ cm}^{-1}$  can be safely assigned to  $\nu(\text{CO})$  of the molecules of the acid bonded to osmocene (molecular complex II). This value is coincident with that for molecular H-complexes of  $\text{CF}_3\text{COOH}$  with organic bases [2]. A rise in temperature is accom-

panied by an increase in the intensity of the  $1790\text{ cm}^{-1}$  band, which, as is well known, is assigned to acid dimers. This band was not observed in the spectral study of the equilibrium between molecular and ionic complexes of halogenacetic acids with organic bases [2,3], because the values of constant formation of the molecular hydrogen bond with organic bases are greater than that with a metal atom [4].

Thus, we have found for the first time that proton transfer from a cationic hydride to an anion can occur in the system of hydrogen-bonded complexes: ionic (I) = molecular (II). The formation of the ionic complex  $[\text{OsH}]^+ \dots \text{A}^-$  takes place before the proton transfer stage.

### 3. Experimental details

All compounds were obtained by known procedures [1]. The spectra were recorded with Specord M-80 and Specord M-82 IR spectrophotometers. Measurements were made in the solid state (KBr) and in  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4/\text{CHCl}_3$  (1:1) solutions. Concentrations were varied in the range 0.1–0.001 mol/l. Solutions of  $\text{K}^+\text{CF}_3\text{COO}^-$  in  $\text{CCl}_4/\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  were prepared in excess of 18-crown-6.

### References

- 1 L.M. Epstein, E.S. Shubina, A.N. Krylov, A.Z. Kreindlin and M.I. Rybinskaya, *J. Organomet. Chem.*, **447** (1993) 277.
- 2 Z. Dega-Szafran and M. Grunvald-Wyspianska, *Spectrochim. Acta*, **47A** (1991) 543.
- 3 G.A. Denisov, G.V. Gusakova and A.I. Smolyansky, *J. Mol. Struct.*, **15** (1973) 377.
- 4 E.S. Shubina, A.N. Krylov, A.Z. Kreindlin, M.I. Rybinskaya and L.M. Epstein, *J. Mol. Struct.*, (1993) in press.