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Hydrogen-bonded complexes involving the metal atom and protonation of metallocenes of the iron subgroup

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Abstract

The interactions were studied of metallocenes and their permethylated analogues of the iron subgroup (M = Fe, Ru, Os) with trifluoroacetic acid in low-polar media. IR and UV-Vis spectra, over a wide temperature range, proved that formation of the molecular hydrogen-bonded complex (OH ··· M) is the first stage of protonation. The ionic H-complexes of the $M^+H \cdots O^-$ type are formed as a result of proton transfer. The influences of the metal, the substituents on the Cp-ring and of the concentration of acid on this acid-base equilibrium are discussed.

Key words: Group 8; Metallocenes; Hydrogen bonding

1. Introduction

Though great attention has been paid to protonation of π-complexes, the mechanism of proton transfer is still unclear. Mass-spectrometric studies of ferrocene protonation have shown that this transfer is unusually slow [1,2]. Hence, the authors have suggested that an intermediate proton-bound ion-molecular complex could exist. We have succeeded in detecting, firstly, ion-molecular ($MH^+ \cdots B$) [3] and, secondly, ionic ($MH^+ \cdots A^-$) [4] hydrogen-bonded complexes, during IR study of the interaction between protonated decamethylosmocene and bases in low-polar media.

The purpose of this work was to examine the role of hydrogen bonds, involving the metal atom, in the protonation of metallocenes. Recently we have characterized molecular hydrogen-bonded complexes formed by phenols with the Ru and Os atoms of the corresponding metallocenes [5]. Metallocenes (Cp_2M) and decamethylmetallocenes (Cp^*_2M) of the iron subgroup (M = Fe, Ru, Os) were therefore chosen for study. Trifluoroacetic acid (TFA) was used as the proton donor. This was for two reasons. Firstly, Cp^*_2Ru and Cp^*_2Os are known to be capable of protonation in an excess of TFA [6]. Secondly, molecular and ionic hydrogen-bonded complexes between this acid and organic bases have been detected in the IR spectra in the range of $\nu(CO)$ and $\nu_a(COO^-)$ vibrations (1820–1620 cm^{-1}) [7]. These spectral characteristics appeared to be appropriate for examination of H-complexes involving the metal atom [4].

We examined the CF_3COOH–metallocene systems by IR and UV-Vis spectroscopy in low-polar media ($CCl_4:CHCl_3$ 1:1, CH_2Cl_2) over a wide range of temperature.

2. Results and discussion

The IR spectroscopy of acid-metallocenes has enabled us to prove the existence of two types of complexes: molecular ($OH \cdots M$) and ionic ($O^- \cdots {}^+[HM]$). Their formation was found to be dependent on concentration ratio and temperature.

If the concentration of the acid is two orders less than that of metallocene (10^{-4} and 10^{-2} mol/l, respectively), the equilibrium observed is of this type:

$$CF_3COOH + [M] \rightleftharpoons \underset{\text{I}}{CF_3COOH \cdots [M]} \rightleftharpoons \underset{\text{II}}{CF_3COO^- \cdots [HM^+]} \qquad (1)$$

The spectra reveal rather weak bands of the "free" acid (1810 cm^{-1} for the monomer and 1790 cm^{-1} for

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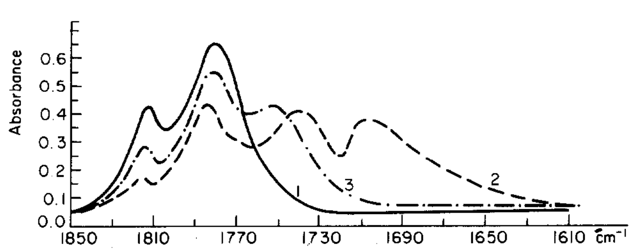


Fig. 1. IR spectra in the ν(CO) range of CF_3COOH (1) ($c = 0.001$ M/l) with Cp^*_2Os (2), CH_3CN (3) ($c = 0.05$ M/l) in CCl_4:CH_2Cl_2 1:1, $d = 1$ mm.

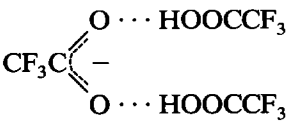
the dimer) and two new bands: 1750–1730 cm^{-1} and 1710–1690 cm^{-1} (Fig. 1). The assignment of the high frequency band to the molecular complex of TFA with the metal atom (1) is based on the agreement with the band arising from the system TFA–CH_3CN (Fig. 1). The proton-accepting ability of the latter bears close similarity to that of Ru and Os atoms in metallocenes [5*]. It should be noted that the bands of molecular complexes of TFA with pyridines are also observed in this range (1750–1720 cm^{-1}) [7].

The assignment of the bands 1710–1690 cm^{-1} to the ionic complex II is based on the proximity of their position to $\nu_a(COO^-)$ of the ionic H-complex TFA-Py (1:1) [7]. The band of the complex $[Cp^*_2OsH]^+ \cdots {}^-OOCCF_3$ is also observed in the immediate vicinity [4].

The equilibrium (1) shifts to the right upon cooling. The "free" acid content decreases, but the number of molecular (I) and ionic complexes (II) increases (Fig. 2). In these conditions the electronic spectra demonstrate the appearance and growth in intensity of the d-d* transition bands, attributed to the protonated metallocenes (Fig. 3a). In the case of Cp^*_2Os, further evidence of the formation of an ionic complex after proton transfer was provided by the appearance and increase in intensity of ν(Os–H) (2200 cm^{-1}) at low temperature (Fig. 3b). The frequency and the shape of this band is closely similar to that of the complex of protonated decamethylosmocene mentioned above [3].

If the concentrations of TFA and metallocenes are equal ($c = 10^{-2}$ mol/l), the equilibrium becomes more complicated.

Novel hydrogen-bonded complexes, *i.e.* acid-anion, were also noted. Based on IR and X-ray data [8], we concluded that these complexes have the symmetric structure:



$$CF_3C\begin{cases} O \cdots HOOCCF_3 \\ O \cdots HOOCCF_3 \end{cases}^{-} \qquad \text{(III)}$$

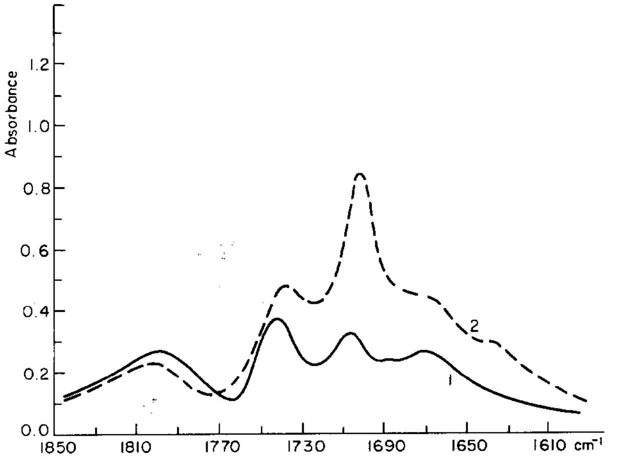


Fig. 2. The temperature dependence of ν(CO) for CF_3COOH ($c = 0.001$ M/l) with Rc^{10} ($c = 0.05$ M/l) in CH_2Cl_2, $d = 1$ mm. 20°C (1), −60°C (2).

A new low-frequency band appears (1630 cm^{-1}), whose intensity is greater than that of the ionic complex II (Fig. 4). It was assigned to a complex with no metallocene, because the spectra of the systems TFA–Cp_2M and TFA–$CF_3COO^-K^+$ (in the presence of 18-crown-6) are similar (Fig. 4). The complex III is evidently more stable than II. Lowering the tempera-

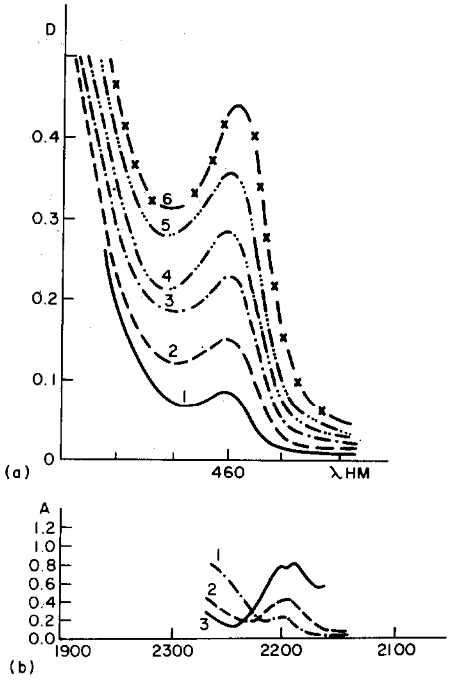


Fig. 3. (a) The temperature dependence of λ d-d* Oc^{10} ($c = 0.01$ M/l) with CF_3COOH ($c = 0.1$ M/l) in CH_2Cl_2, $d = 1$ mm. 20°C (1), 0°C (2), −20°C (3), −40°C (4), −60°C (5), −80°C (6). (b) The temperature dependence of ν(MH) for Oc^{10} ($c = 0.05$ M/l) with CF_3COOH ($c = 0.05$ M/l) in CH_2Cl_2, $d = 3$ mm. 20°C (1), −20°C (2), −60°C (3).

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* Reference number with an asterisk indicates a note in the list of references.

ture causes the increase in intensity of the 1630 cm^{-1} band (complex III) and the disappearance of the band that was in the range 1705–1690 cm^{-1}. Equilibrium (2) shifts to the right.

$$\underset{\substack{\nu(CO)\ 1810\\ 1790}}{CF_3COOH} + MCp^*_2 \rightleftharpoons \underset{\substack{1750\text{–}1730\\ \text{I}}}{CF_3COOH\cdots MCp^*_2} \rightleftharpoons$$

$$\underset{\substack{1705\text{–}1690\\ \nu(OsH^+)\ 2200\\ \text{II}}}{CF_3COO^-\cdots{}^+HMCp^*_2} \rightleftharpoons$$

$$\underset{\substack{1630\\ \text{III}}}{CF_3COO^-\cdots(HOOCCF_3)_2} + Cp^*_2MH \qquad (2)$$

We have found the effects of the nature of the metal atom and of methylation of the Cp-ring on proton transfer (equilibrium (2)).

A decrease in intensity of TFA bands is caused by formation of molecular and ionic complexes, which proceed more easily in the series (Fig. 5):

$$Cp_2Ru < Cp_2Os < Cp^*_2Ru < Cp^*_2Os \qquad (3)$$

Such a series could be obtained from the data on the formation of molecular complexes with phenols [5]. As can be seen from (3), the effect of the electron-donating ability of the substituents in the Cp-ring can be equal to or greater than that of the metal atom ($Cp_2Os < Cp^*_2Ru$).

With regard to the iron atom, the question of the site of protonation of Cp_2Fe in the gas phase remains unsolved [1,2]. As is known, the formation of the hydrogen bond between ferrocene and proton donors, which are weaker than TFA, occurs only on the Cp-ring [5].

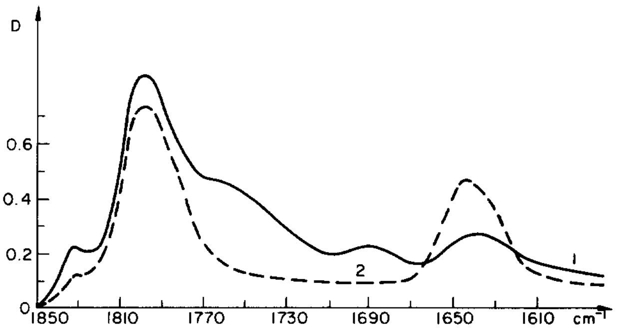

Fig. 4. IR spectra in the ν(CO) range of CF_3COOH (c = 0.01 M/l) with Cp^*_2Os (1) (c = 0.02 M/l) and $CF_3COO^+K^-$ (c = 0.02 M/l) with 18-crown-6 in CH_2Cl_2, d = 1 mm.

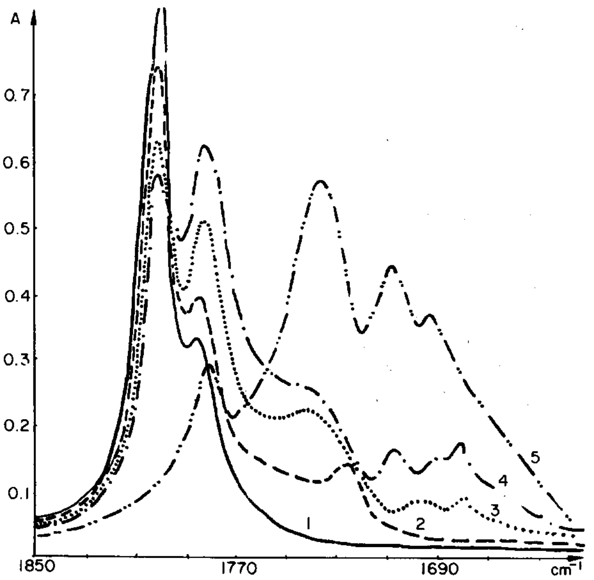

Fig. 5. IR spectra in the ν(CO) range of CF_3COOH (1) (c = 0.001 M/l) with Rc(2), Oc(3), Cp^*_2Ru(4). Cp^*_2Os(5) (c = 0.05 M/l) in CH_2Cl_2 d = 1 mm.

We have succeeded in detecting the molecular H-bonded complex of OH ⋯ Fe type as well as the ionic complex $O^- \cdots [HFe]^+$ for the system TFA-Cp_2Fe at low temperature (−60°C). The intensities of the bands attributed to these complexes are, naturally, less than those of Cp_2Ru or Cp_2Os, but we found only a quantitative difference. All these data are indicative of there being a common mechanism for proton transfer which involves the prior hydrogen bonding of OH ⋯ M type for all metallocenes of the iron subgroup.

Thus, we have found that the first stage of protonation of the metallocenes in low-solvating media is the formation of the molecular H-bonded complex with the metal atom (OH ⋯ M). The proton transfer should be accompanied by the formation of the ionic complex of the protonated metallocene and the anion of this acid ($[MH]^+ \cdots O^-$).

3. Experimental section

The compounds studied were prepared by published procedures [6].

The IR spectra were recorded with Specord M-80 and M-82 instruments. Measurements were made in CH_2Cl_2 and $CH_2Cl_2:CCl_4$ (1:1) solutions. The concentrations of the bases (Fc, Rc, Oc, Rc^{10}, Oc^{10}) were varied in the range 7×10^{-2}–5×10^{-3} mol/l, concentrations of the proton donor (CF_3COOH) were 5×10^{-3}–1×10^{-2} mol/l, d = 0.01–0.04 cm. The temperature dependence (295–215 K) was investigated in CH_2Cl_2 under argon. The ν(OH) values correspond to their centres of gravity (s = 4 cm^{-1}).

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