The Energy Profile of Proton Transfer from Brønsted Acids to Terminal Hydrides in Transition Metal Complexes Can Be Estimated by Combining in situ IR and NMR Spectroscopy

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Keywords: Hydrides / Hydrogen bonding / Rhenium / IR spectroscopy / NMR spectroscopy

The enthalpy and entropy changes relative to the stepwise reaction of [(triphos)Re(CO)$_2$H] with perfluoro-*tert*-butyl alcohol in CH_2Cl_2 to give first the hydrogen-bonded adduct [(triphos)Re(CO)$_2$H···HOC(CF$_3$)$_3$] and then the stable non-classical dihydrogen complex [(triphos)Re(CO)$_2$(η^2-H$_2$)]$^+$ have been estimated by a combination of in situ IR and NMR experiments in the temperature range from 200 to 260 K [triphos = MeC(CH$_2$PPh$_2$)$_3$].

Introduction

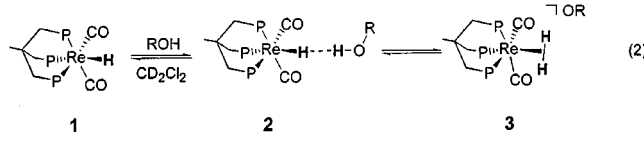
The reactions of hydrido metal complexes with Brønsted acids yielding cationic nonclassical η^2-H$_2$ derivatives have been interpreted for a long time as proceeding straightforwardly by proton attack at terminal hydride ligands.[1] Experimental evidence for an alternative, stepwise, mechanistic picture has recently been provided, however. This involves the intermediacy of H-bonded species prior to H_2 ligand formation, as shown in Equation (1). In particular, the use of protic acids of different strength has allowed the interception and unambiguous characterisation of several H-bonded [MH]···HX species.[2,3]

$$\text{M-H} \rightleftharpoons \text{M-H}\cdots\text{HO-R} \rightleftharpoons \text{M-(H}_2\text{)} \qquad (1)$$

The enthalpy values associated with the formation of the H-bonded adducts have been determined for some systems in nonpolar or low-polarity solvents.[2a–2c,3b,3c] In contrast, the thermodynamic parameters relative to the M−H···H−OR → M−(η^2-H$_2$) step have only been reported for the reaction of the dihydride *trans*-[RuH$_2$(dppm)$_2$] (dppm = diphenylphosphanylmethane) with phenol in toluene.[3a] Unexpectedly large enthalpy (17 kcal mol^{-1}) and entropy (75.8 e.u.) values were obtained.[3a]

Results and Discussion

In this communication, we show that the energy associated with each stage of the proton transfer process in Equation (1), as well as the overall energy involved, can be calculated using a combined IR and NMR approach. To this purpose, the interaction of the Re^{III} hydride [(triphos)Re(CO)$_2$H] (**1**) [triphos = MeC(CH$_2$PPh$_2$)$_3$][4] with perfluoro-*tert*-butyl alcohol (PFTB) was studied in dichloromethane. We chose **1** for the simple reason that some data relative to the equilibrium shown in Equation (2) were already available.[3b,3c]



(2)

It may be useful to recall here that the η^2-H$_2$ complex [(triphos)Re(CO)$_2$(η^2-H$_2$)]$^+$ (**3**) is completely stable from 200 to 260 K in CH_2Cl_2.[3c,4] In this temperature range, the occurrence of a dynamic equilibrium involving the three species shown in Equation 2 was unambiguously demonstrated; moreover, the enthalpy values relative to the formation of several H-bonded adducts of the formula [(triphos)Re(CO)$_2$H···HOR] were calculated from IR spectroscopy using the Iogansen equation $-\Delta H = 18\Delta\nu/(720 + \Delta\nu)$.[2a,3b] For ROH = PFTB, a medium strength H-bonded adduct **2** was obtained with an enthalpy value of 6.0 kcal mol^{-1}.[3c]

The overall energy gain involved in the proton transfer reaction **1** → **3** has now been calculated from the temperature dependence of the protonation constant K_{1-3} for the equilibrium illustrated in Equation 2 [c(**1**) = 5 × 10^{-3} M, c(PFTB) = 5 × 10^{-2} M]. The values of K_{1-3} = [**3**]/[**2**+**1**] were determined from significant intensity changes of the ν_{sym}(CO) band at 2005 cm^{-1} of **3**. Figure 1 shows that this

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  1434−1948/00/1010−2163 $ 17.50+.50/0

band is well separated from any other band in the region, while the ν(CO) bands of **2** (1930 and 1984 cm^{-1}) overlap with those of **1**, and the first band of **2** is partially masked by ν_{asym}(CO) of **3** at 1940 cm^{-1}. The values $-\Delta H°_{1-3}$ = 8.3 ± 0.4 kcal mol^{-1}, $-\Delta S°_{1-3}$ = 31.6 ± 1.8 e.u. were determined from a plot of $\ln K_{1-3}$ vs. $1/T$ (Table 1) in the temperature range from 200 to 260 K.

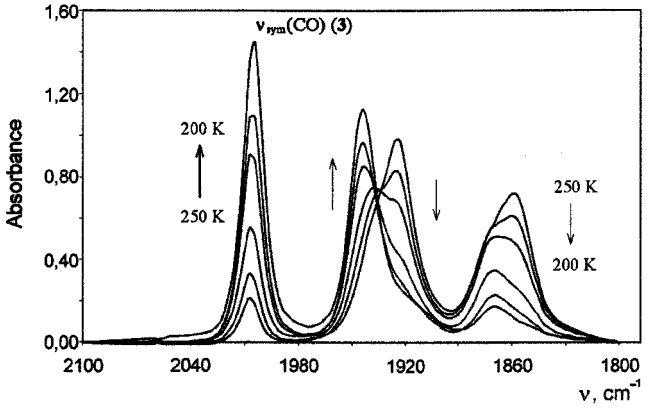


Figure 1. Variable-temperature IR spectra (ν_{CO} range) of complex **1** (0.005 M) in the presence of a 10-fold excess of PFTB in the temperature range between 250 and 200 K (interval 10 K)

Table 1. Values of formation constants K_{1-3} and K_{2-3} obtained from IR and NMR spectroscopic data, respectively

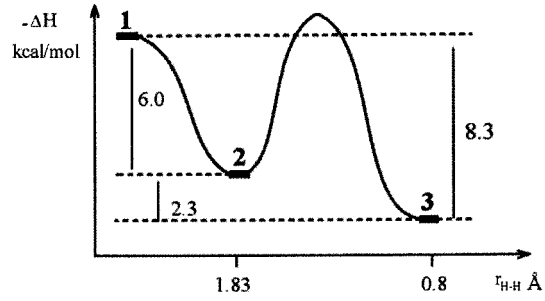
T, K	K_{1-3}	*T*, K	K_{2-3}
200	176.6	200	5.2
210	43.4	230	2.8
220	24.8	240	1.7
230	9.5	260	1.4
240	4.5		
250	2.5		

A ^{1}H NMR analysis in CD_2Cl_2 for the system **1**/PFTB has allowed us to calculate the energy associated with the formation of **3** from **2**. The equilibrium constants K_{2-3} for this reaction were determined at several temperatures in the 200−260 K range from the integral intensities of the hydride signals of **3** (−4.8 ppm) and **2** (−6.28 ppm). For a large excess of alcohol (e.g. 10 equivalents of PFTB), there is no free **1** at 200 K and therefore the equilibrium constant K_{2-3} between **2** and **3** can easily be calculated. The molar fractions of the H-bonded species **2** at higher temperatures were calculated from the observed average chemical shifts using a standard procedure.[3c] From this study, the enthalpy ($-\Delta H°_{2-3}$ = 2.3 kcal mol^{-1}) and entropy ($-\Delta S°_{2-3}$ = 8.4 e.u.) associated with the transformation of **2** into **3** were thus estimated.

As reported above, the enthalpy relative to the formation of **2**, determined independently by IR spectroscopy,[3c] is 6.0 kcal mol^{-1}. Adding this value to the value of 2.3 kcal mol^{-1}, obtained for the **2** → **3** conversion by NMR spectroscopy, gives a total $-\Delta H°$ of 8.3 kcal mol^{-1} for the **1** + PFTB → **3** reaction, which is identical to the enthalpy calculated by IR methods for the same process.

In conclusion, we have shown here that the energy profile of a proton-transfer reaction involving an H-bonded intermediate can reliably be evaluated by a combination of independent IR and NMR experiments.

Scheme 1 illustrates the energy profile for the transformation of **1** into **3** *via* **2**. The potential energy curve shows two minima: the first is due to the formation of the H-bonded species with r = 1.83 Å[3c] while the lower energy one is due to the thermodynamically favoured η^2-H_2 complex **3**, for which an H−H distance of 0.81 Å was previously reported assuming fast rotation of the H_2 ligand.[4]



Scheme 1. Energy profile for the transformation of **1** into **3** via **2**.

The energetic level of the transition state for the **2** → **3** conversion is shown only qualitatively in Scheme 1, while that for the formation of **2** is not even shown as the formation of H-bonded adducts is a diffusion-controlled process.[5] Indeed, the transformation of **2** into **3** is too slow on the NMR timescale (10^1−10^{-6} s) and separated hydride signals for the two compounds were observed with no broadening of the resonances over the range of temperature investigated. Accordingly, the reaction has a lifetime longer than 10 s, which in turn provides an upper limit of 10^{-1} s^{-1} for the rate constant. The lower limit of the rate constant may be estimated roughly considering that our IR technique does not allow one to monitor the band intensity changes for processes faster than 10^{-2} s^{-1} (it takes one minute for mixing the reagents and loading the sample into the cryostat). Since no intensity change with time was observed, it could be assumed that the lifetime of the proton transfer is shorter than 1−2 min, which provides a lower limit of 10^{-2} s^{-1} for the rate constant.[6] It may be thus concluded that the transformation of **2** into **3** presumably proceeds with a rate constant between 10^{-2} and 10^{-1} s^{-1} with an activation barrier $\Delta G^{‡}$(200 K) from 12 to 13 kcal mol^{-1}. This estimate falls within the ranges reported in the literature (10^{-4}−10^{-1} dm^3 mol^{-1} s^{-1}; 1−40 kcal mol^{-1}).[7,8]

Experimental Section

All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques. Dichloromethane was distilled from CaH_2 prior to use. All IR and NMR measurements were carried out as previously described.[3c] Complex **1** was prepared as reported in the literature.[4]

Acknowledgments

Thanks are due to NATO (contract *"^{2}H-Relaxation as a tool to study hydrogen transfer reactions"*, grant HTECH-CRG 972135), CNR/RAS agreement and RFBR (project No 99−03−33270) for financial support.

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Received April 7, 2000
[I00136]