

The Effect of the "Inert" Counteranions in the Deprotonation of the Dihydrogen Complex $trans\text{-}[\text{FeH}(\eta^2\text{-H}_2)(\text{dppe})_2]^+$: Kinetic and Theoretical Studies

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In the past few years there is growing evidence that shows the formation of stable ion pairs involving metal hydride and dihydrogen complexes and different anions.^{1,2} However, most work to date has dealt with the structural features of these ion pairs, and no report has been made on their effect on the kinetic properties of the complexes, despite the fact that ion pairing has been shown to influence the reaction rate for other coordination compounds.³ In the present communication, we report on the kinetics of deprotonation by NEt_3 of the dihydrogen complex $trans\text{-}[\text{FeH}(\text{H}_2)(\text{dppe})_2]^+$ (**1**) ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) and demonstrate that ion pairing leads to drastic kinetic changes, the reaction being accelerated or decelerated depending on the nature of the anion. Complex **1** has a pK_a (12–13)⁴ close to that of NEt_3 (10.8), and thus, reaction 1 is expected to be displaced to the right only in the presence of a large excess of base. NMR experiments in acetone and thf solutions confirm that the addition of an excess of NEt_3 causes the complete conversion of $[\mathbf{1}](\text{BF}_4^-)$ to $cis\text{-}[\text{FeH}_2(\text{dppe})_2]$ (**2**) and show that the process occurs without accumulation of any reaction intermediate.⁵



Stopped-flow experiments yield kinetic traces that can be well fitted by a single exponential, the observed rate constant increasing linearly with the concentration of amine (Figure 1a) and yielding a second-order rate constant of $0.18 \text{ M}^{-1} \text{ s}^{-1}$. When the kinetic measurements are carried out in the presence of added Bu_4NBF_4 , the results are surprising because ionic strength effects are usually small for reactions involving a neutral reagent,⁶ and reaction 1 is accelerated by a factor of 10 ($k = 1.68 \text{ M}^{-1} \text{ s}^{-1}$, see Figure 1b). Moreover, the effect is strongly dependent on the nature of the anion because Bu_4NPF_6 only increases slightly the second-order rate constant to a value of $0.27 \text{ M}^{-1} \text{ s}^{-1}$ and NaBPh_4 causes a significant decrease of the rate of reaction.⁷ As the stopped-flow experiments showed a clear effect of added anions on the reaction kinetics, the NMR experiments were repeated in the presence of added salts to confirm that the nature of the reaction product remains the same.

These results show clearly that the anion plays an active role in the deprotonation process, probably through the formation of an adduct with some kind of interaction with the dihydrogen ligand. To obtain information about these interactions, the relaxation time of the H_2 ligand in **1** was measured at different temperatures in the presence of the salts used in the kinetic studies. Although the added salts only cause negligible changes in the $T_{1\text{min}}$ values, the temperature at which the minimum is achieved increases in the

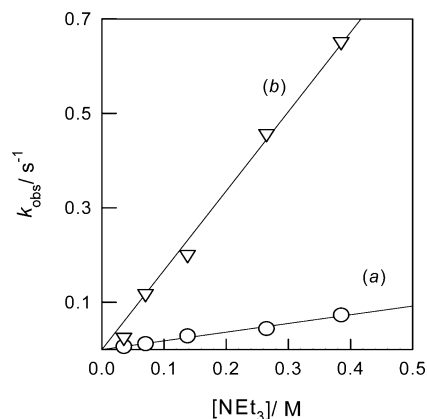


Figure 1. The dependence of the observed rate constant (25 °C, dry thf solvent, Ar atmosphere) upon base concentration for the reaction of $[\mathbf{1}](\text{BF}_4^-)$ ($2.0 \times 10^{-4} \text{ M}$) with NEt_3 in the absence of added electrolyte (a) and in the presence of $5.0 \times 10^{-2} \text{ M}$ Bu_4NBF_4 (b).

presence of any of the salts, in agreement with a longer correlation time caused by adduct formation.⁸ However, these experiments do not show any difference when the nature of the anion is changed.

The ^1H NOESY spectrum of a solution of **1** with added NaBPh_4 shows that the phenyl protons of the anion interact with both the hydride and the dihydrogen ligands, which indicates that BPh_4^- approaches the complex in the directions of these ligands, thus imposing severe steric constraints to the approach of the base and causing a deceleration of the deprotonation process. Unfortunately, ^{19}F , ^1H HOESY experiments were unsuccessful in detecting any interaction between the protons of **1** and the BF_4^- anion, probably because the short relaxation times of the H^- and H_2 ligands and the fluorines in the anion cause the decay of any possible NOE during the mix time of the HOESY experiments. In the absence of information on the nature of the interaction between the H_2 ligand and BF_4^- , DFT calculations were carried out on this interaction and its role on the deprotonation process. To simplify the calculations, the model complex $trans\text{-}[\text{FeH}(\text{H}_2)(\text{dhpe})_2]^+$ (**1b**) ($\text{dhpe} = \text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2$) and NMe_3 were used instead of **1** and NEt_3 .⁹

Calculations were initially carried out considering exclusively the **1b** cation and NMe_3 , and the results are summarized in Figure 2. Deprotonation occurs through the initial formation of adduct **3** with a short H–H distance (0.810 Å), followed by reorganization to give a species **4** that can be described as a *trans*-dihydride/protonated amine adduct, although the interaction is quite uncommon because it involves the formation of a strong dihydrogen bond with a quasi-linear arrangement of the $\text{Fe}\cdots\text{H}\cdots\text{H}\cdots\text{N}$ unit and a short H \cdots H distance (1.211 Å). The energy difference between **3** and **4** is quite small, but the overall deprotonation process is not

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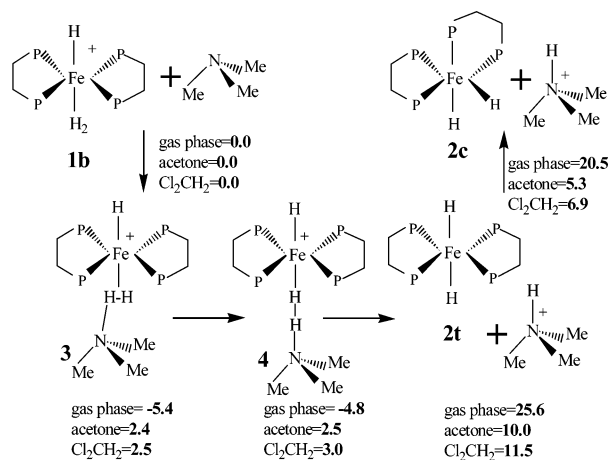


Figure 2. Reaction energies (kcal/mol), in gas phase, acetone, and dichloromethane, of the several steps of the $\mathbf{1b} + \text{NMe}_3 \rightarrow \text{cis-}[\text{FeH}_2(\text{dppe})_2] + \text{HNMe}_3^+$ process.

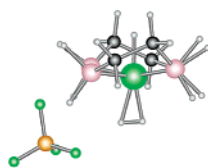


Figure 3. Optimized structure of the (**1b**, BF_4^-) ion pair.

avored because the release of $\text{trans-}[\text{FeH}_2(\text{dppe})_2]$ (**2t**) and HNMe_3^+ from **4** is highly endothermic. Although the subsequent isomerization to **2c** causes a stabilization, the overall process is still unfavorable.

When one BF_4^- anion is included in the calculations, an ion pair is formed between **1b** and BF_4^- , the anion interacting preferentially with the H_2 ligand (Figure 3). This ion pair then interacts with the base with the sequential formation of two adducts **5** and **6** with structures similar to **3** and **4**, except that there is now an additional interaction with the anion that is maintained through the whole deprotonation process (see Supporting Information). From **6**, the process continues with separation of the trans- dihydride and an $(\text{HNMe}_3^+, \text{BF}_4^-)$ ion pair, followed by isomerization to the cis- dihydride. The breaking of **6** requires less energy than in the absence of BF_4^- . For instance, the products **2c** + HNMe_3^+ are found 3.9 kcal/mol above **4** in dichloromethane, whereas **2c** + $(\text{HNMe}_3^+, \text{BF}_4^-)$ lie 5.4 kcal/mol below **6**. BF_4^- follows the proton along its transfer. Thus, it can be concluded that the role of the anion in the deprotonation process consists mainly in favoring the separation of the reaction products through the formation of a stable $(\text{HNMe}_3^+, \text{BF}_4^-)$ ion pair. From the mechanistic point of view, the acceleration observed in the presence of added BF_4^- would be then caused by the operation of a more favorable reaction pathway that goes through ion pairs. This explanation clearly differs from that previously proposed to explain the accelerating effect of small anions on the deprotonation of $[\text{MoH}(\text{CO})_2(\text{diphosphine})_2]\text{BF}_4$, for which a mechanism has been proposed in which the anions act as proton carriers from the sterically hindered proximity of the metal center to the amine.¹⁰

The accelerating effect is expected to be very dependent on the nature of the anion. The reaction pathway through the ion pairs will be effective only when the three starting species (**1**, the base, and the anion) can approach each other, and the phenyl groups in the dppe ligands impose serious steric constraints not considered in the calculations.

The deceleration observed for BPh_4^- indicates that the large size of this anion hinders the approach of the base to the (**1**, BPh_4^-)

ion pair and the reaction must go through the free-ion pathway: as the concentration of free **1** is very small in the presence of an excess of BPh_4^- , the reaction is largely decelerated.

The results in the present report clearly show the relevance of ion-pair formation in the kinetic properties of the dihydrogen complexes. It is evident that for charged complexes, ion pairing will be a general phenomenon in the solvents commonly used to study these complexes, and thus, special care must be taken to consider the possible effects of the usually considered “inert” counterions when examining the reactivity of these species.

Acknowledgment. Financial support by the Spanish DGI (Projects BQU2000-232 and BQU2002-04110-CO2-02) and Junta de Andalucía (Grupo FQM-137) is gratefully acknowledged. Partial support from the EC-RTN project “Hydrochem” (HPRN-CT-2002-00176) is also acknowledged.

Supporting Information Available: Experimental and computational details and tables of the optimized geometries (Cartesian coordinates) for the **1b** to **4** calculated species; optimized structures of **5**, **6**, and (**1b**, BPh_4^-) (PDF). This material is available free of charge via Internet at <http://pubs.acs.org>.

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- It has been previously shown that formation of hydrogen-bonded adducts of $\text{RuH}(\text{H}_2)\text{L}(\text{PCy}_3)_2$ ($\text{L} = \text{C}_5\text{H}_4\text{N-X}$, $\text{X} = \text{O}, \text{NH}$) with hydrogen bond donors does not change T_{min} but leads to longer correlation times, in agreement with formation of association complexes: Guari, Y.; Ayllon, J. A.; Sabo-Etienne, S.; Chaudret, B.; Hessen, B. *Inorg. Chem.* **1998**, *37*, 640.
- DFT calculations with the B3LYP functional. Computational details are given in the Supporting Information.
- The kinetic features are also different in both cases. For the Mo complex, deprotonation is accelerated by small anions, but the rate law changes from a first-order dependence on the concentration of base to a first-order dependence on the anion concentration. In contrast, deprotonation of **1** is accelerated because of an increase of the second-order rate constant: (a) Hanckel, J. M.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1983**, *105*, 6979. (b) Darensbourg, M. Y.; Ludvig, M. M. *Inorg. Chem.* **1986**, *25*, 2894.

JA039844J