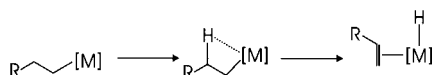


# Inherent Asymmetry of Constitutionally Equivalent Methyl Groups in the H/D Equilibration of *n*- and *i*-C<sub>3</sub>H<sub>7</sub>Fe(OH)<sup>+</sup> Complexes\*\*

Claudia Trage, Waltraud Zummack, Detlef Schröder, and Helmut Schwarz\*

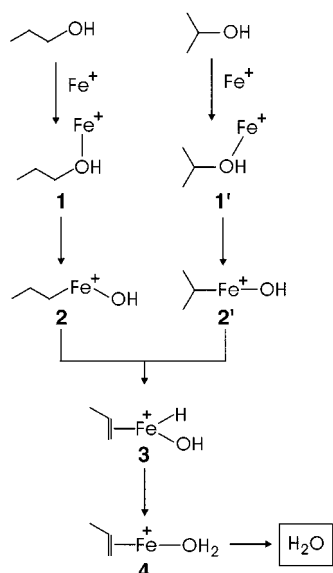
Dedicated to Graham Cooks  
on the occasion of his 60th birthday

Reversible  $\beta$ -hydrogen transfer, a key reaction in organo-metallic chemistry, often relies on an alignment of the alkyl residue in terms of an agostic interaction (Scheme 1). Here,



Scheme 1. Reversible  $\beta$ -hydrogen transfer with an agostic interaction.

we report that in the course of an *n*-propyl  $\rightleftharpoons$  isopropyl isomerization, operative in Fe<sup>+</sup>-mediated dehydration of propanols, the transiently formed constitutionally identical methyl groups remain inequivalent. In general, water loss is



Scheme 2. Schematic reaction pathway for the loss of water from [Fe/propanol]<sup>+</sup>.

believed to commence with complexation of the metal cation at oxygen, followed by oxidative insertion into the C–O bond (Scheme 2: **1**  $\rightarrow$  **2** or **1'**  $\rightarrow$  **2'**).<sup>[1, 2]</sup> Next,  $\beta$ -hydrogen transfers lead to either a hydrido hydroxy complex **3** or directly<sup>[3]</sup> to the bisligated complex **4**; the latter decomposes preferentially by loss of water, because H<sub>2</sub>O is less strongly bound to Fe<sup>+</sup> than propene.<sup>[4]</sup> In fact, the metastable ions **1** and **1'** show almost exclusive elimination of water (> 99%) on the microsecond time scale.<sup>[6]</sup> The key question concerns the reversibility of the  $\beta$ -hydrogen transfer steps **2**  $\rightleftharpoons$  **2'**, which is addressed by examination of the H/D equilibration in unimolecular reactions of metastable complexes of Fe<sup>+</sup> with a set of selectively deuterated propanols<sup>[7]</sup> by using tandem mass spectrometry.<sup>[8, 9]</sup>

Inspection of the experimental data in Tables 1 and 2 leads to three immediate conclusions: 1) extensive H/D equilibration is observed, 2) the complexes of labeled *n*- and isopropanol show distinctly different H<sub>2</sub>O/HDO ratios, and 3) the hydroxy groups of **1** and **1'** do not participate in the H/D scrambling. While metal-mediated H/D equilibrations have been observed frequently, such cases are often described only phenomenologically, rather than analyzed rigorously.<sup>[10]</sup>

Table 1. H<sub>2</sub>O/HDO losses from metastable complexes of Fe<sup>+</sup> with labeled isopropanols.

| Substrate                                | Experiment <sup>[a]</sup> |                       | Model A <sup>[b]</sup> |       | Model B <sup>[c]</sup> |       | Statistical <sup>[d]</sup> |       |
|------------------------------------------|---------------------------|-----------------------|------------------------|-------|------------------------|-------|----------------------------|-------|
|                                          | H <sub>2</sub> O          | HDO                   | H <sub>2</sub> O       | HDO   | H <sub>2</sub> O       | HDO   | H <sub>2</sub> O           | HDO   |
| CH <sub>3</sub> CH(OD)CH <sub>3</sub>    | < 1 <sup>[e]</sup>        | > 99                  | 0.0                    | 100.0 | 0.0                    | 100.0 | 0.0                        | 100.0 |
| CH <sub>3</sub> CD(OH)CH <sub>3</sub>    | 94.9                      | 5.1                   | 95.4                   | 4.6   | 94.9                   | 5.1   | 85.7                       | 14.3  |
| CH <sub>3</sub> CH(OH)CD <sub>3</sub>    | 73.4                      | 26.6                  | 70.7                   | 29.3  | 73.0                   | 27.0  | 57.1                       | 42.9  |
| CH <sub>2</sub> DCD(OH)CH <sub>2</sub> D | 77.1                      | 22.9                  | 75.8                   | 24.2  | 77.3                   | 22.7  | 57.1                       | 42.9  |
| CHD <sub>2</sub> CH(OH)CHD <sub>2</sub>  | 58.6                      | 41.4                  | 56.6                   | 43.4  | 59.0                   | 41.0  | 42.9                       | 57.1  |
| CD <sub>3</sub> CH(OH)CD <sub>3</sub>    | 14.9                      | 85.1                  | 16.4                   | 83.6  | 14.9                   | 85.1  | 14.3                       | 85.7  |
| CD <sub>3</sub> CD(OH)CD <sub>3</sub>    | < 0.7                     | > 99.3 <sup>[f]</sup> | 0.0                    | 100.0 | 0.0                    | 100.0 | 0.0                        | 100.0 |

[a] Averaged intensities obtained in three independent experiments normalized to  $\Sigma = 100$ . The experimental error is less than  $\pm 0.8$ . [b] Parameters:  $k_{\text{sel}} = 0.381$  and  $\text{KIE} = 2.02$ . [c] Parameters:  $k_{\text{sel}} = 0.515$ ,  $\text{KIE}_{\text{sel}} = 2.33$ , and  $\text{KIE}_{\text{ex}} = 2.24$ . [d] Calculated by assuming statistical distribution of all seven H/D atoms of the C<sub>3</sub>H<sub>7–n</sub>D<sub>n</sub> units. [e] Upper limit of H<sub>2</sub>O loss derived from analysis of the MI spectra of CH<sub>3</sub>CH(OD)CH<sub>3</sub>/Fe<sup>+</sup> at various degrees of O-deuteration (due to H/D exchange in the inlet system). [f] Lower limit of HDO loss derived from analysis of the noise level in the MI spectra of CD<sub>3</sub>CD(OH)CD<sub>3</sub>/Fe<sup>+</sup>.

Table 2. H<sub>2</sub>O/HDO losses from metastable complexes of Fe<sup>+</sup> with labeled *n*-propanols.

| Substrate                                           | Experiment <sup>[a]</sup> |                       | Model B <sup>[b]</sup> |       | Model C <sup>[c]</sup> |       | Statistical <sup>[d]</sup> |       |
|-----------------------------------------------------|---------------------------|-----------------------|------------------------|-------|------------------------|-------|----------------------------|-------|
|                                                     | H <sub>2</sub> O          | HDO                   | H <sub>2</sub> O       | HDO   | H <sub>2</sub> O       | HDO   | H <sub>2</sub> O           | HDO   |
| CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OD  | < 2 <sup>[e]</sup>        | > 98                  | 0.0                    | 100.0 | 0.0                    | 100.0 | 0.0                        | 100.0 |
| CH <sub>3</sub> CH <sub>2</sub> CD <sub>2</sub> OH  | 82.6                      | 17.4                  | 86.4                   | 13.6  | 83.0                   | 17.0  | 71.4                       | 28.6  |
| CH <sub>3</sub> CD <sub>2</sub> CH <sub>2</sub> OH  | 79.5                      | 20.5                  | 81.3                   | 18.7  | 80.3                   | 19.7  | 71.4                       | 28.6  |
| CH <sub>2</sub> DCHDCH <sub>2</sub> OH              | 85.4                      | 14.6                  | 83.7                   | 16.3  | 84.8                   | 15.2  | 71.4                       | 28.6  |
| CHD <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH | 89.1                      | 10.9                  | 86.4                   | 13.6  | 88.8                   | 11.2  | 71.4                       | 28.6  |
| CH <sub>2</sub> DCHDCHDOH                           | 75.0                      | 25.0                  | 74.6                   | 25.4  | 73.7                   | 26.3  | 57.1                       | 42.9  |
| CD <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH  | 81.2                      | 18.8                  | 77.0                   | 23.0  | 82.0                   | 18.0  | 57.1                       | 42.9  |
| CD <sub>3</sub> CD <sub>2</sub> CH <sub>2</sub> OH  | 50.3                      | 49.7                  | 46.8                   | 53.2  | 50.3                   | 49.7  | 28.6                       | 71.4  |
| CD <sub>3</sub> CD <sub>2</sub> CD <sub>2</sub> OH  | < 0.4                     | > 99.6 <sup>[f]</sup> | 0.0                    | 100.0 | 0.0                    | 100.0 | 0.0                        | 100.0 |

[a] Averaged intensities obtained in three independent experiments normalized to  $\Sigma = 100$ . The experimental error is less than  $\pm 0.8$ . [b] Parameters:  $k_{\text{sel}} = -0.033$ ,  $\text{KIE}_{\text{sel}} = -0.250$ , and  $\text{KIE}_{\text{ex}} = 2.24$ . [c] Parameters:  $k_{\text{sel}} = 0.068$ ,  $\text{KIE}_{\text{sel}} = 2.72$ , and  $\text{KIE}_{\text{ex}} = 2.25$ ,  $f_{\text{as}} = 0.7$ . [d] Calculated by assuming statistical distribution of all seven H/D atoms of the C<sub>3</sub>H<sub>7–n</sub>D<sub>n</sub> units. [e] Upper limit of H<sub>2</sub>O loss derived from analysis of the MI spectra of CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OD/Fe<sup>+</sup> at various degrees of O-deuteration (due to H/D exchange in the inlet system). [f] Lower limit of HDO loss derived from analysis of the noise level in the MI spectra of CD<sub>3</sub>CD<sub>2</sub>CD<sub>2</sub>OH/Fe<sup>+</sup>.

Herein we present such a quantitative analysis.<sup>[11]</sup> We begin with isopropanol **1'** as the analysis is more simple due to the constitutional equivalence of the methyl groups. At first, we assume that  $\beta$ -H and  $\beta$ -D transfers are associated with a kinetic isotope effect (KIE). Irrespective of the chosen KIEs, however, the experimental data systematically deviate from statistical H/D equilibration, such that a certain degree of a specific 1,2-elimination ( $k_{\text{sel}}$ ) needs to be included. Thus, for the description of the H<sub>2</sub>O/HDO ratios for isopropanol/Fe<sup>+</sup>,

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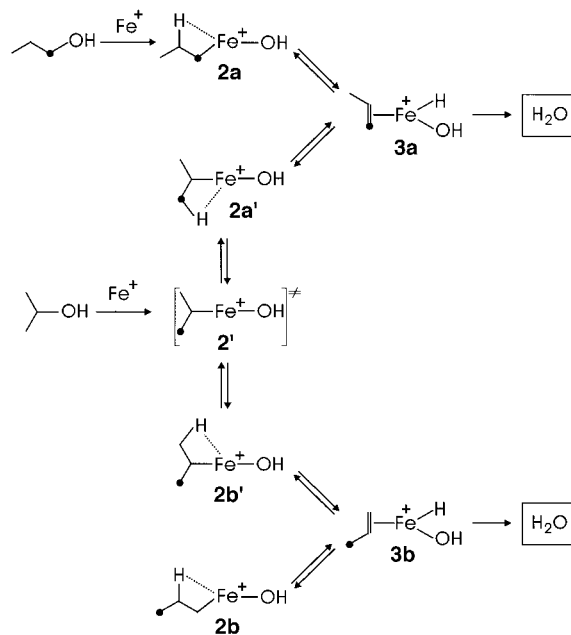
[\*\*] We thank the Volkswagen-Stiftung, the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie for generous funding.

we end up in a system of kinetic equations with KIE and  $k_{\text{sel}}$  as parameters (model **A**). While this two-parameter model, in which the same KIE is employed for the specific and unspecific paths, yields a reasonable fit of the experimental ratios, some discrepancies remain. Significant improvement is obtained, if one differentiates between the KIEs of the selective 1,2-elimination and of the exchange reaction, that is, using  $k_{\text{sel}}$ ,  $\text{KIE}_{\text{sel}}$ , and  $\text{KIE}_{\text{ex}}$  as variables (model **B**). With these three parameters, the experimental data can be modeled within the experimental error.<sup>[12]</sup> In summary, the data suggest that the sequence  $2 \rightleftharpoons 2'$  is partially reversible with an irreversible outlet via **4** to the products; the latter conclusion is based on the lack of participation of the OH group in H/D exchange.<sup>[13]</sup> We note in passing that H/D exchange is also absent for the bisligated complex  $[(\text{C}_3\text{D}_6)\text{Fe}(\text{H}_2\text{O})]^+$  generated independently by chemical ionization (CI) of  $[\text{Fe}(\text{CO})_5]$ ,  $\text{H}_2\text{O}$ , and  $[\text{D}_6]\text{propene}$ .

Application of model **B** to the *n*-propanol/ $\text{Fe}^+$  system results in poor agreement between experimental and modeled data and, more importantly, unrealistic parameters, for example,  $k_{\text{sel}} < 0$ , emerge. Prior to any discussion of the appropriateness of the models (numerical inaccuracies etc.), the experimental data clearly indicate that *another* variable is required. The comparison of the  $[\text{D}_2]$  isotopomers is most instructive in this respect. Thus, the  $\text{H}_2\text{O}/\text{HDO}$  ratios for the  $[1,1\text{-D}_2]$  and  $[2,2\text{-D}_2]$  compounds are very similar, though not identical, indicating almost complete scrambling of the H/D atoms of the methylene groups. However, the  $[2,3\text{-D}_2]$ - and  $[3,3\text{-D}_2]$  isotopologues show significantly lower amounts of HDO losses; in fact, it takes the  $[3,3,3\text{-D}_3]$  sample to reach the  $\text{H}_2\text{O}/\text{HDO}$  ratios of the  $[1,1\text{-D}_2]$  and  $[2,2\text{-D}_2]$  compounds. Accordingly, while the H/D atoms at C1 and C2 undergo almost complete scrambling, the terminal methyl group participates to a lower extent. This conclusion is, however, in obvious contradiction to an H/D equilibration in alkyl metal compounds by reversible  $\beta$ -hydrogen transfer (see Scheme 2), because it would imply a *n*-propyl to isopropyl isomerization without an isopropyl intermediate! In other words, the classical view of an involvement of an isopropyl moiety with two constitutionally equivalent methyl groups contradicts the experimental findings. Therefore, an asymmetry factor  $f_{\text{as}}$  is introduced as an additional parameter (model **C**). This parameter describes the nonequivalency of the C1 and C3 positions in the conversion  $2 \rightleftharpoons 2'$ . Model **C** provides a reasonable fit of the experimental data which is not as perfect as in the isopropanol/ $\text{Fe}^+$  system, but is inside the error margins of the experiment. A key point to be made is that the asymmetry of the C1 and C3 positions is still visible in the product formation, even though the KIEs  $> 2$  indicate that  $\beta\text{-H(D)}$  transfer contributes to the rate-determining step.

Kinetic modeling of elementary reactions, however, only provides numbers and no chemical insight. What kinds of structural effects could cause asymmetry between the existing and the emerging methyl groups as in the isomerization of a propyl unit? A clue is provided by the hypothesis that metal cation binding to alkyl fragments bearing  $\beta$ -hydrogen atoms is inherently associated with an agostic interaction; in fact, structures without agostic interactions are no minima, but saddle points.<sup>[15]</sup> Accordingly, the central part of Scheme 2 is

extended in Scheme 3, where C1 of *n*-propanol is deliberately marked by a dot. For *n*-propanol/ $\text{Fe}^+$ , equilibration of the H/D atoms at C1 and C2 could occur through the reversible



Scheme 3. Extended model for the loss of water from  $[\text{Fe}/\text{propanol}]^+$  considering the nonequivalency of the two methyl groups.

sequence  $2\text{a} \rightleftharpoons 2\text{a}'$ . Participation of the original C3 position is, however, only achieved through the classical structure  $2'$ , which is assumed to be a transition structure for the degenerate interconversion  $2\text{a}' \rightleftharpoons 2\text{b}'$ . The experimentally shown nonequivalence of the C1 and C3 positions in the H/D equilibration of *n*-propanol/ $\text{Fe}^+$  further suggests that the related barrier is sufficiently high to compete with the irreversible hydrogen transfer to the hydroxy group ( $3 \rightarrow 4 \rightarrow \text{products}$ ).

The inherent asymmetry of alkyl metal compounds assumed is, perhaps, of more general relevance as it may also help to understand some of the puzzling results obtained in olefin hydrogenation, for example, isotopically scrambled products having a uniform stereochemistry,<sup>[16]</sup> as well as the diastereoselectivity of transition metal and metallocene-catalyzed olefin polymerization.<sup>[17]</sup> Further mechanistic studies as well as a theoretical examination of this challenging problem are in progress.

Received: April 25, 2001 [Z 16994]

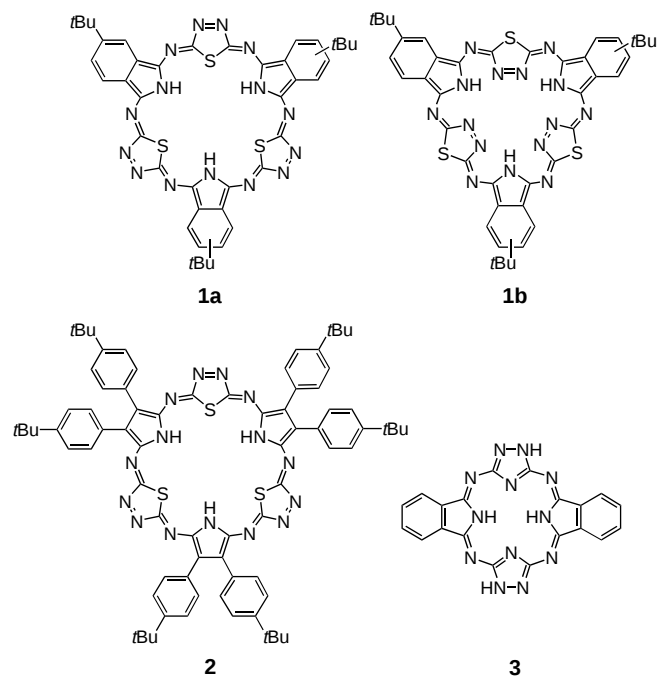
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- [8] The experiments were performed with a modified VG ZAB/HF/AMD four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sectors) which has been described previously.<sup>[9]</sup> Briefly, propanol/ $\text{Fe}^+$  complexes were generated by chemical ionization of a mixture of  $[\text{Fe}(\text{CO})_5]$  and the corresponding propanol. The ions were accelerated to 8 keV kinetic energy and mass-selected by means of B(1)/E(1) at a resolution of  $m/\Delta m \approx 3000$ . Unimolecular fragmentations of metastable ions occurring in the field-free region preceding B(2) were recorded by scanning this sector. A total of 10 to 30 scans were averaged to improve the signal-to-noise-ratio, and the data are the averages of at least three independent measurements.
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- [12] Note that secondary kinetic isotope effects need not be considered explicitly, because they are either inherently included in the analysis or cancel out in the  $\text{H}_2\text{O}/\text{HDO}$  ratios.
- [13] Additional information, which will be presented in a full article, suggests that the C–O bond insertion  $1 \rightarrow 2$  is also quasi-irreversible for the metastable ions. This conclusion is further supported by the substantial barrier predicted for the insertion of  $\text{Fe}^+$  into the C–O bond of methanol.<sup>[14]</sup>
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## A Novel Hemiporphyrizine Comprising Three Isoindolediimine and Three Thiadiazole Units\*\*

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Large aromatic macrocyclic compounds such as porphyrins and phthalocyanines have attracted the interest of many chemists.<sup>[1, 2]</sup> In the phthalocyanine family, naphthalocyanines are important analogues and have been used in commercial fields such as read/write compact discs. Although not often used in practice, perhaps the next best known phthalocyanine analogues are hemiporphyrazines, which can be obtained by the condensation reaction of equimolar amounts of 1*H*-isoindole-1,3(2*H*)-diimines and 2,6-diaminopyridines.<sup>[3]</sup> Around a decade ago, a new member, synthesized from 1*H*-isoindole-1,3(2*H*)-diimines and 2,5-diamino-1,3,4-triazoles, was introduced into this family, and now such hemiporphyrazines are conventionally known as triazole hemiporphyrazine **3** (Scheme 1).<sup>[4]</sup> These compounds are cyclic tetramers



Scheme 1. Two possible structures **1a** and **1b** for the condensation products of 2,5-diamino-1,3,4-thiadiazole and 5-*tert*-butylisoindolediimine, and a possible structure for compound **2**. The triazole hemiporphyrazine structure is shown at the bottom right.

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[\*\*] This work was supported partly by a Grant-in-Aid for Scientific Research (B) No. 11440192 and the Shorai Foundation for Science & Technology.

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