4. Regio- and Stereoselectivity of Transition-Metal-Ion-Mediated Single and Double Dehydrogenation of Tetraline

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Labeling experiments provide evidence that the Fe^I- and Co^I-mediated losses of H_2 and 2 H_2 from tetraline are extremely specific in that both reactions follow a clear *syn*-1,2-elimination involving C(1)/C(2) and C(3)/C(4), respectively. In the course of the multi-step reaction, the metal ions do not move from one side of the π-surface to the other. Independent experiments confirm that the kinetic isotope effect (KIE) associated with the loss of the first H_2 molecule is indeed larger than the KIE for the elimination of the second H_2 molecule.

While there exist numerous reports on the reactions of 'bare' and partially ligated transition-metal ions with organic substrates in the gas phase [1], detailed studies on the stereochemical course of the metal-mediated C–H bond activation are scarce[2]. Among the conditions which have to be met in order to meaningfully apply stereochemical criteria to, for example, the dehydrogenation of a CH_2CH_2 group, the two most important ones are: *i*) reductive loss of molecular hydrogen is not preceded by hydrogen scrambling, and *ii*) H-atom transfer from the alkyl chain to the metal centre is regiospecific.

Here, we report on our results on the Fe^I- and Co^I-mediated single and double dehydrogenation of tetraline in the gas phase[3][4], and we shall demonstrate that these

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[2] For a recent study on the regioselectivity, stereoselectivity, and isotopically sensitive branching in the Fe^I-mediated dehydrogenation of octane-1,8-diol in the gas phase, see [2].

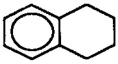
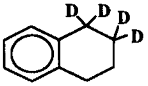
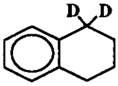
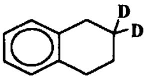
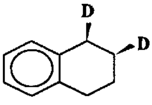
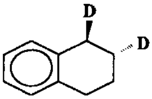
[3] For an early, however not fully conclusive mechanistic study on the dehydrogenation of cyclohexadiene/ $Fe(CO)_x^+$ complexes ($x = 1, 2$) in the gas phase, see [3].

[4] As the experimental set-up has been described repeatedly [4], a brief description may suffice: A 1:5 to 10 mixture of $Fe(CO)_5$ (or $Co(CO)_3NO$) and tetraline is bombarded with 100-eV electrons in the chemical ionization source (repeller voltage 0 V) of a modified four-sector tandem mass spectrometer of *BEBE* configuration (*B* stands for magnetic and *E* for electric sector), in which MS-I is the original *ZAB-2F* part and MS-II is an *AMD 604* mass spectrometer [5]. Although the actual mechanisms by which the complexes are formed is yet unknown, the pressure in the ion source is high enough to permit collisional cooling, thus, increasing the lifetime such that time-delayed decomposition reactions after *ca.* 1 µs take place (metastable ion (MI) dissociations). To this end, the organometallic complexes of M^+ (M = Fe, Co) and tetraline (and its isotopomers) having 8-keV translational energy are mass-selected by means of $B(1)E(1)$. Unimolecular reactions occurring in the field-free region between $E(1)$ and $B(2)$ were recorded by scanning $B(2)$. In these experiments, the fourth sector $E(2)$ is not used. However, an $E(2)$ scan was employed in an MS/MS experiment in which the dehydrogenation product of $B(1)E(1)$ mass-selected precursors was 'isolated' by means of $B(2)$, and the second dehydrogenation occurring in the fourth field-free region was monitored by scanning $E(2)$. Spectra were recorded on-line and averaged by using signal-averaging techniques employing the *AMD Intectra* data system. In typical experiments, 10–15 spectra were recorded. All compounds were synthesized by standard laboratory procedures [6], purified by chromatographic means, and fully characterized by spectroscopic methods.

reactions are both *regio*- and *stereo*specific. In addition, the kinetic isotope effects associated with the metal-ion-mediated loss of molecular hydrogen are reported.

In the *Table*, the MI data for the Fe^+- and Co^+-complexes of tetraline (**1**) and its isotopomers **1a–e** are given. For both metal ions, there are only two reactions taking place which correspond to the single and double dehydrogenation. A kinetic modelling reveals that the relative rates for the second over the first dehydrogenation step amounts to 125 for the Fe^+ system and 72 for the Co^+ complex, respectively. Further, in contrast to the MI mass spectrum of tetraline itself[5]), in the organometallic complexes **1-M**$^+$ (M = Fe, Co) no products due to C–C bond activation are formed.

Table. *Unimolecular Single and Double Dehydrogenation of* Fe^+ *and* Co^+ *Complexes of Tetraline* (**1**) *and Its Isotopomers* **1a–e**[a])

Precursor		Δm					Kinetic Isotope Effect (KIE) of Dehydrogenation	
		2	3	4	5	6	1st	2nd
	**1**	35 (52)		65 (48)				
	**1a**	37 (46)		8 (13)		55 (41)	3.4 ± 0.2[d]) 3.0 ± 0.2[d])	1.5 ± 0.2[e]) 1.4 ± 0.2[e])
	**1b**	29 (37)	12 (19)		59 (44)		1.9 ± 0.2[e]) 1.7 ± 0.2[e])	1.3 ± 0.2[e]) 1.3 ± 0.2[e])
	**1c**	29 (35)	11 (19)		60 (46)		2.1 ± 0.2[e]) 2.0 ± 0.2[e])	1.3 ± 0.2[e]) 1.1 ± 0.2[e])
	**1d**[b])	41 (49)		43[c]) (36)[c])		16 (15)		
	**1e**[b])	31 (38)	12 (19)		57 (43)		1.9 ± 0.2[e]) 1.9 ± 0.2[e])	1.5 ± 0.2[e]) 1.2 ± 0.2[e])

[a]) Data are given in % of Σ fragment intensities = 100; the numbers given in parentheses refer to the Co^+-induced reactions.

[b]) **1d** and **1e** have been studied as racemic pairs.

[c]) Δm = 4 can, in principle, correspond to the loss of D_2 or the combined elimination of H_2/H_2 (see text).

[d]) KIE = $k(H_2)/k(D_2)$.

[e]) KIE = $k(H_2)/k(HD)$.

The investigation of the labeled tetralines **1a–e** provides unambiguous evidence that both metal ions bring about *regio*- and *stereo*specific activation for either the first and the

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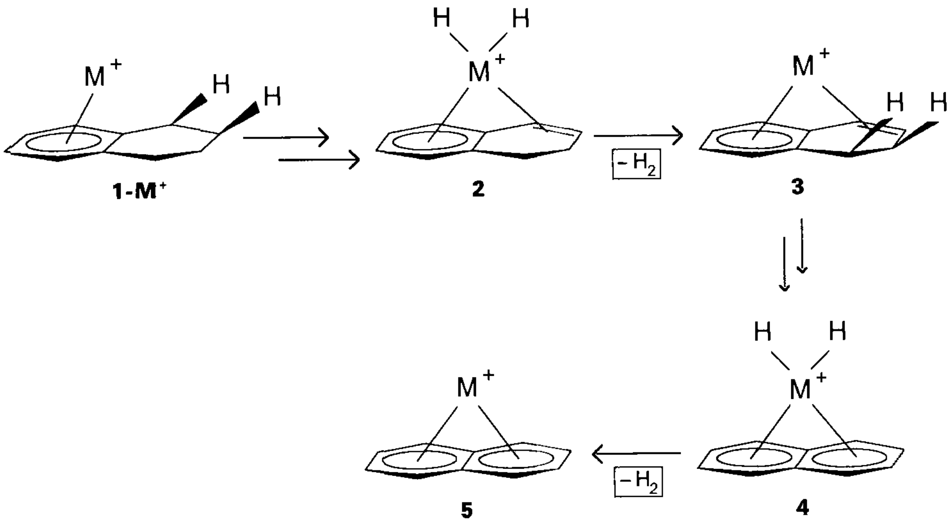
[5]) In the MI mass spectrum of **1**, we observe the following losses: Δm = 1 (1 %), 2 (1), 15 (12), 28 (83), 40 (1), and 41 (2).

second dehydrogenation. The losses of molecular hydrogen, originating exclusively from C(1)/C(2) and C(3)/C(4) (see data for **1a**–**1c**), clearly point to a reaction which eventually leads to a naphthalene-metal complex **5**[6]). From the study of **1b** and **1c**, we further conclude that Fe^+-mediated activation of a benzylic or homobenzylic C–H bond is *not* associated with the rate-determining step. From the practically identical isotope distributions in the competitive formations of H_2/HD and the combined losses of H_2 and HD, one has to conclude that the observed kinetic isotope effects originate from the reductive elimination step of molecular hydrogen. Information on the stereochemical course of the C–H bond activation (oxidative insertion of M^+ in the C–H bond as well as β-H transfer) and in particular on the question as to whether the metal ion sticks to the same plane of the hydrocarbon surface is provided by the data of the racemic mixtures of compounds **1d** and **1e**, respectively. The fact that the metal-complexes of the *cis*-labeled tetraline undergo *no* loss of HD, while the MI mass spectra of the *trans*-complexes **1e-M**$^+$ (M = Fe, Co) contain signals for both H_2 and HD elimination (but not for D_2) convincingly demonstrates that *i*) in the overall reaction the metal ion does not switch from one π-surface to the other, and *ii*) the H (D) atom transfer to the metal centre follow a *syn*-process. An over-simplified picture of the reaction is depicted in the *Scheme*[7]).

The kinetic isotope effects (KIE)[8]) associated with the first and second dehydrogenation steps (**1-M**$^+$→**3** and **3**→**5**, respectively) are different and being larger for the elimination of the first molecule of hydrogen. While there exist several conceivable mechanistic scenarios to account for this observation, we have sought for further experiments to

Scheme



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[6]) Our supposition that 'aromatization' is a driving force in the sequential M^+-mediated dehydrogenation is supported by the observation that the MI spectra of the Fe^+ and Co^+ complexes of indane and benzosuberane contain only a signal due to loss of H_2.

[7]) The actual nature of the interaction of M^+ with the hydrocarbon surface cannot be inferred from the present experiments and remains unknown.

[8]) The KIE were calculated using the standard procedures for a system of parallel and consecutive reactions.

underline our supposition that the differences in KIE reflect primarily the interaction of the metal ion with the hydrocarbon π-surface in that in the final step an arene-M^+ complex is formed. To this end, we have performed an experiment in which the two dehydrogenation steps were studied individually. For a model of the first dehydrogenation, we have investigated the Fe^+-mediated dehydrogenation of ethylbenzene (**6**) and its isotopomers $PhCHDCH_3$ (**6a**) and $PhCH_2CHD_2$ (**6b**). The kinetic isotope effects for the side-specific losses[9]) of H_2 *vs.* HD from these precursors are as follows: for **6a** $k(H_2)/k(HD) = 1.8$; for **6b** $k(H_2)/k(HD) = 2.0$. The KIE associated with the Fe^+-mediated loss of the second hydrogen molecule from tetraline is probed by subjecting **1d** to the following MS/MS experiment: the complex **1d-Fe$^+$** is mass-selected by $B(1)/E(1)$, the product due to unimolecular loss of H_2 is formed in the third field-free region and is 'isolated' by $B(2)$, and the ratio of H_2 *vs.* D_2 is determined by scanning $E(2)$. We observe a kinetic isotope effect $k(H_2)/k(D_2) = 1.5 \pm 0.1$ which is in excellent agreement with the data for **1a** in the *Table.*

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[4] a) T. Prüsse, H. Schwarz, *Organometallics* **1989,** *8,* 2856; b) T. Prüsse, Ph.D. Thesis, Technische Universität Berlin, D83, 1991.

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[6] A. Heesing, W. Müllers, *Chem. Ber.* **1980,** *113,* 9.

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[9]) The MI mass spectrum of **6-Fe$^+$** exhibits only a signal due to loss of molecular hydrogen, and the investigation of **6a** and **6b** demonstrates that the molecule is formed exclusively in a formal 1,2-elimination from the Et side chain.