41. Dehydration of Alkanones by Bare FeO^+ Involves the $\omega/(\omega - 1)$ Positions: Exclusion of Iron Carbenes as Intermediates

Preliminary Communication

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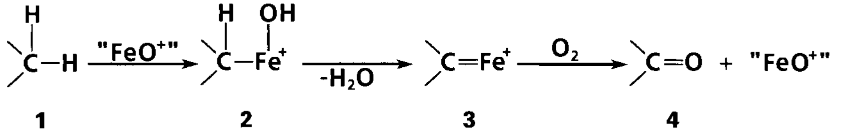
Fourier-transform ion-cyclotron-resonance (FTICR) mass spectrometry has been used to uncover the mechanisms by which FeO^+ dehydrates heptan-4-one (**5a**) and nonan-5-one (**6a**) in the gas phase. The study of isotopomeric ketones provides evidence that H_2O loss is not due to a 1,1-elimination, thus ruling out the intermediacy of high-valent iron-carbene species. Rather, H_2O is generated in a formal 1,2-elimination involving the $\omega/\omega - 1$ positions of the alkyl chain ('remote C–H bond activation'). In the consecutive alkene/H_2O elimination, the olefins (ethylene from **5a** and propene from **6a**) originate from the terminal part of one alkyl chain, and the H-atom is transferred to the FeO^+ moiety in the course of this process, builds up together with an H-atom from the $\omega/\omega - 1$ position of the *other* alkyl chain the H_2O molecule. In either case, the O-atom of H_2O is provided by the FeO^+ species.

Iron-catalyzed hydrocarbon oxidation is a field of great scope and economic volume [1]. However, the understanding of the mechanisms by which C–H bonds of alkanes are functionalized is – in spite of the progress over the last three decades – far from being complete [1b]. The current understanding is quite advanced in the case where the catalyst is an iron-porphyrin, and there exists good evidence that such reactions occur *via* high-valent iron-oxo intermediates $(Fe(V)O)^+$ [2][1]. One of the most intriguing *non-enzymatic* oxygenation systems was discovered by *Barton* and coworkers and has been referred to by them as the 'Gif IV' system [2h] [3]. Detailed examination led them to propose that iron carbenes **3**, formed by oxidative addition of a C–H bond to a high-valent ionic '$Fe{=}O^{+}$' species, are the central intermediates in the course of ketone formation from alkanes *(Scheme 1)*.

Scheme 1



It should, however, be noted that the groups of *Geletii* and *Shilov* [4] proposed a different explanation. According to these authors, the real oxidant is an *iron-free* pyridine-oxide radical cation, which inserts an O-atom in a CH_2 group to generate

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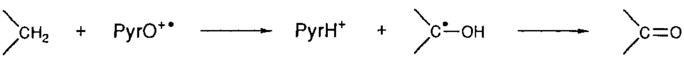
[1] For an excellent collection of papers on this and related topics, see the special (October–November) issue of *New J. Chem.* **1989**, *13*. Of particular importance in this context are the following contributions: [1b] [2d–j].

Scheme 2



C-centred radicals which further evolve into the major oxidized products, *i.e.* ketones *(Scheme 2)*.

Although it is difficult to reconcile the *Geletii-Shilov* mechanism with *all* experimental findings, it should also be recalled that there exists no firm experimental evidence for any of the intermediates described in *Scheme 1*. In fact, the exact nature of the metal-ion containing intermediates that are suggested to be involved in the oxidation of alkanes is by and large unknown [2g].

Previous studies (for reviews, see [5]) have already demonstrated that more detailed mechanistic information on reactions of ionic transition-metal oxides MO^+ (M = Fe, V, Cr, Os) [6] with simple hydrocarbons can be obtained free from any interference due to aggregation, solvent and counter-ion effects, if the processes are conducted in the dilute gas phase.

Here, we present an account of the reactions of *bare* FeO^+ with acyclic ketones²) using the technique of *Fourier*-transform ion-cyclotron-resonance mass spectrometry (FTICR). The apparatus (a *Spectrospin-CMS-47X* equipped with an external ion source) and its operation have been described in detail in [8]. Briefly, Fe^+ is formed *via* laser desorption/ionization [9] in the external ion source [10] by focussing the beam of a *Nd:YAG* laser *(Spectron Systems,* fundamental frequency 1064 nm) onto a stainless steel rod. The ions are extracted from the source and transferred into the analyzer cell by a system of electric potentials and lenses. After deceleration, the ions are trapped in the field of the superconducting magnet *(Oxford Instruments)*, which has a maximum field strength of 7.05 Tesla. The $^{56}Fe^+$ isotope is isolated *via* swept double-resonance ejection pulses and allowed to react for 2 s with pulsed-in N_2O to generate FeO^+ [6a, b]. As this reaction is exothermic by *ca.* 1.8 eV [11], the products are formed with some excess energy which is carried away by collisionally cooling the system using Ar at a constant background pressure of *ca.* 10^{-7} mbar. The FeO^+ species was again 'isolated' and then reacted with the ketones of interest. The latter were present at a pressure of $1–5 \times 10^{-8}$ mbar. Typical reaction time was 1–5 s. All functions of the instrument were controlled by a *Bruker-Aspect-3000* mini-computer.

The labeled compounds were synthesized according to standard procedures, purified by preparative GC, and characterized by spectroscopic methods.

For the reactions of FeO^+ with heptan-4-one (**5a**) and nonan-5-one (**6a**), we observed, as primary products, the species given in *Scheme 3*. Insight into the mechanisms of their formation is provided by the study of the isotopomers **5b–f** and **6b–e** *(Table)*. Here, we shall restrict the discussion to the losses of H_2O and alkene/H_2O. The remaining reactions will be reported in a full paper.

With regard to H_2O loss, the labelling data provide an unequivocal answer concerning the positions from which the neutral molecule originates. From the study of the ^{18}O-

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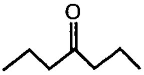
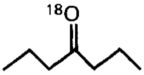
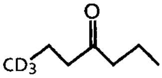
²) The reactions of Fe^+ with acyclic ketones, including *inter alia* the successive C–H/C–C bond activation of *different* segments of the two alkyl chains, were recently investigated [7].



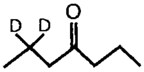
5a



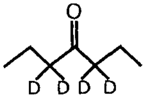
5b



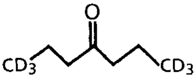
5c



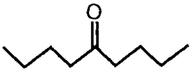
5d



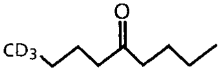
5e



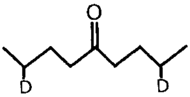
5f



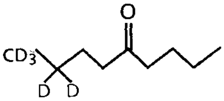
6a



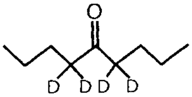
6b



6c

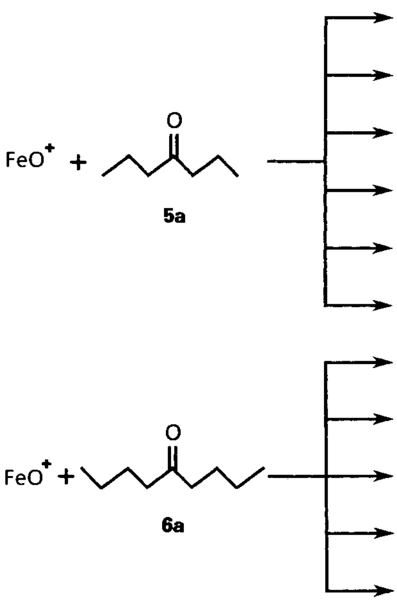


6d



6e

Scheme 3



Ion	Neutral	Relative abundance [%]
$FeC_7H_{12}O^+$	H_2O	6
$FeC_7H_{10}O^+$	H_2O/H_2	2
$FeC_5H_8O^+$	C_2H_4/H_2O	19
$FeC_3H_6O_2^+$	C_2H_4/C_2H_4	12
$FeC_4H_8^+$	$[C_2H_4/H_2O/CO]$	13
$FeC_3H_6^+$	$[H_2O/CO/C_3H_6]$	48
$FeC_9H_{16}O^+$	H_2O	19
$FeC_6H_{10}O^+$	C_3H_6/H_2O	17
$FeC_3H_6O_2^+$	C_3H_6/C_3H_6	9
$FeC_4H_8^+$	$[H_2O/CO/C_4H_8]$	40
$FeC_4H_6^+$	$[H_2O/CO/C_4H_8/H_2]$	15

Table. *Losses of H_2O, C_2H_4/H_2O, and C_3H_6/H_2O from the FeO^+ Complexes of Heptan-4-one* (**5a**) *and Nonan-5-one* (**6a**) *and Their Isotopomers*[a])

	Δm												
	'H_2O'[b])			'C_2H_4/H_2O'					'C_3H_6/H_2O'				
	18	19	20	46	47	48	49	50	60	61	62	63	65
5a	100			100									
5b	100			100									
5c	85	15		40	25		35						
5d	83	17		21	26	53							
5e	100			100									
5f		100					86	14					
6a	100								100				
6b	75	25							30	30		40	
6c	76	24								82	18		
6d	68	18	14						23	39			38
6e	100								100				

[a]) Intensities are expressed in %-Σ fragments = 100%, for each class of neutrals separately.

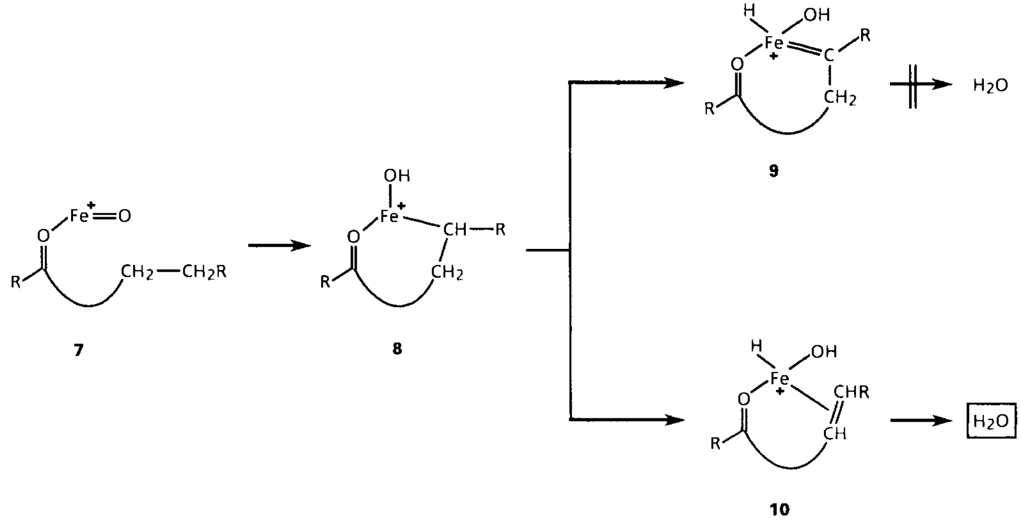
[b]) In the spectra of **5**-FeO^+, contributions for combined losses of H_2O/H_2 and their isotopomers are omitted for the sake of clarity.

labeled substrate **5b**, we note that the C=O O-atom is not incorporated into the neutral molecule. We further note that for the heptan-4-one system **5**-FeO^+, the H-atoms orginate from the $\omega/\omega - 1$ positions of the alkyl chain. Thus, remote functionalization is operative (for reviews, see [12]). Interestingly, we do not observe products due to 1,1-elimination of H_2O; rather the H_2O molecule is generated in a formal 1,2-elimination reaction. *This finding rules out the intermediacy of an iron-carbene species* **9** *(cf. Scheme 4)*; instead, the labelling results are consistent with the formation of a bidentate complex **10**. Incidentally, the latter is also formed with high selectivity in the dehydrogenation of ketones by Fe^+ [7]. The behavior of the nonan-5-one/FeO^+ complexes **6**-FeO^+ is by and large analogous to that of its lower homologue **5**-FeO^+. Common to both systems are also the quite large kinetic isotope effects associated with the generation of H_2O. This was also observed in many oxidations of alkanes catalyzed by high-valent iron-oxo species [2e]. A mechanism, which is in line with the experimental findings, is suggested in *Scheme 4*.

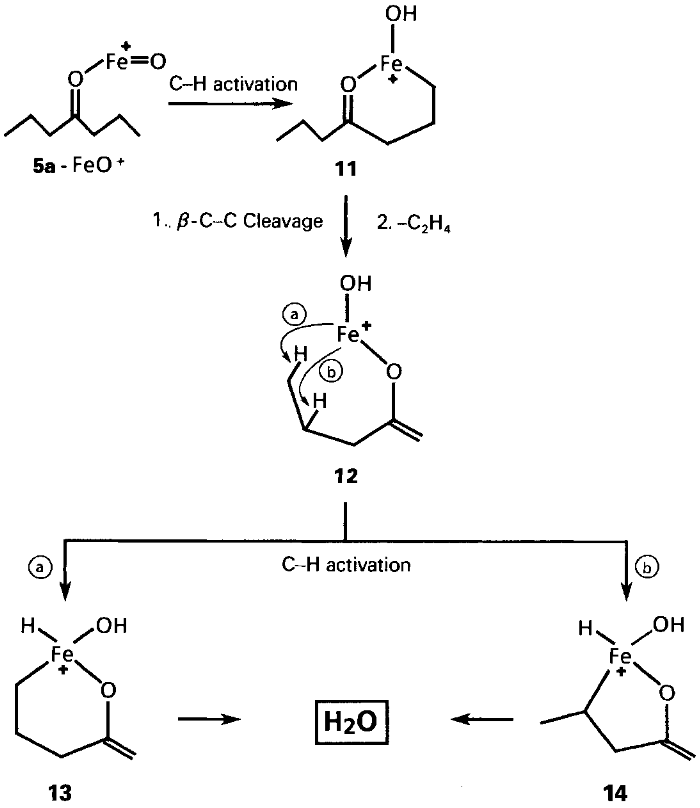
We also note the close analogy of this dehydration to the *dehydrosulfurization* observed in the butane-isothiocyanate/Fe^+ system [13]. Loss of H_2S commences with sulfur abstraction and affords a butane-isocyanide/FeS^+ intermediate which also abstracts H from the $\omega/\omega-1$ positions of the alkyl chain. In this as well as in the present system, reaction intermediates are generated in which a FeX^+ moiety (X = O, S) is 'anchored' to a substrate and specifically activates the remote $\omega/\omega - 1$ positions to eventually yield H_2X.

The consecutive losses of alkene/H_2O from **5** and **6** cannot be accounted for in terms of *Scheme 4*, as far as H_2O elimination is concerned. Instead, another variant is operative. The labeling data reveal that the alkenes (C_2H_4 and C_3H_6, respectively) are formed, with large specifity, from the terminal part of one alkyl chain ('remote functionalization'). Most interestingly, the H-atom transferred to the FeO^+ moiety of the complex in the course of this reaction *(Scheme 5;* **5a**–$FeO^+ \rightarrow$ **11**) is eventually incorporated in the H_2O molecule. The second H-atom is provided by the *other* alkyl chain; for the heptan-4-one system the ω and $\omega - 1$ position serves as an H source; for the nonan-5-one complexes, in

Scheme 4



Scheme 5



addition, the ($\omega - 2$) position contributes to some extent. Unknown kinetic isotope effects prevent a quantitative assignment of the site specificity. In *Scheme 5*, a possible reaction sequence is depicted for the heptan-4-one-FeO^+ system. We should like to point out that the consecutive alkene/H_2O losses constitute a further example for the activation of different sites of flexible molecules by ionic transition-metal systems [7] [14].

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