167. Unimolecular Gas-Phase Oxidation of Terminal Hydroxy Groups in $[FeO(CH_2)_nOH]^+$ Complexes ($n = 2$–8). A Case for O–H Bond Activation by Late Transition-Metal Ions

Preliminary Communication

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In contrast to Fe^+/diol complexes, gas-phase dehydrogenation of the corresponding Fe^{II} alkoxides, $[FeO(CH_2)_nCH_2OH]^+$, is a highly specific process in the course of which oxidation of the terminal OH group takes place. Based on labeling studies, this is the exclusive mechanism for $n = 2$ and 3 (*Scheme*: path ⓐ); for higher homologues, as for example $[FeO(CH_2)_7CH_2OH]^+$, the labeling data demonstrate that an additional mechanism is operative, involving the dehydrogenation of internal positions of the alkyl chain (path ⓑ). The Fe^+-mediated oxidation $-CH_2OH \rightarrow -CHO + H_2$ constitutes one of the rare examples of O–H bond activation by late cationic transition-metal ions.

If mixtures of aliphatic diols, $HO(CH_2)_nOH$ ($n = 2$–8), and $Fe(CO)_5$ are bombarded with 100-eV electrons in the chemical ionization source of a four-sector BEBE mass spectrometer¹), in addition to $[Fe(ROH)]^+$ complexes, we observe intense signals corresponding to Fe^{II} alkoxides, $[Fe(OR)]^+$ [2]; labeling experiments demonstrate [2] that the H-atom lost specifically originates from the OH group of the diol²). If the $[Fe(OR)]^+$ ions are mass-selected by B(1)E(1) and their unimolecular reactions, occurring in the field-free region between E(1) and B(2), recorded by means of B(2), one obtains metastable ion (MI) mass spectra (*Table 1*) which are distinctly different from those of the corresponding $[Fe(ROH)]^+$ complexes [2]. For the latter, it was observed that dehydrogenation is absent for substrates $HO(CH_2)_nOH$ with $n = 2$–5, and detailed labeling studies [2] [4] revealed for $n > 5$ that molecular hydrogen originates from the *central part* of the CH_2 chain separating the two OH groups. For example, in the Fe^+-mediated dehydrogenation of $HO(CH_2)_8OH$ *ca.* 80% of H_2 is provided by C(4)/C(5) and the remaining 20% by C(3)/C(4) and its equivalent C(5)/C(6) positions. This high selectivity reflects the propensity of Fe^+ to intramolecularly activate C–H bonds by 'remote functionalization' [5] favoring five- and six-membered metallacyclic intermediates for $[Fe(ROH)]^+$ complexes [2] [4] [6]. Consequently, for shorter alcohols, this mechanism is no longer favored, and other processes, like H_2O loss, dominate [2]. Obviously, the abundant dehydrogenation reported in *Table 1* for *all* Fe^{II} alkoxides, $[FeO(CH_2)_nOH]^+$ ($n = 2$–8), immediately suggests that another mechanism is operative.

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¹) For a detailed description and operation of the machine, see [1].

²) For the unique, bimolecular chemistry of Fe^{II} alkoxides with ketones, a gas-phase analogue of the well-known *Meerwein-Ponndorf-Verley-Oppenauer* reaction, see [3].

Table 1. *Metastable-Ion (MI) Mass Spectra of $[FeO(CH_2)_nOH]^+$ Complexes*[a])

n in Precursor $HO(CH_2)_nOH$	Neutral (*Δm*) eliminated				
	H_2 (2)	H_2O (18)	C_2H_4 (28)	CH_2O (30)	C_3H_6 (42)
2	56	44			
3	61	26	13		
4	35	43		6	16
5	69	15		16	
6	59	31	5	5	
7	75	14	8	3	
8	67	14		5	4

[a]) Data are expressed in Σ fragments = 100%.

Table 2. *Metastable-Ion (MI) Mass Spectra of Fe^+ Alkoxide Complexes of Diol Isotopomers*[a])

Precursor	*Δm*											
	2	3	4	18	19	20	28	30	32	42	44	46
$HOCD_2CH_2CD_2OH$		15		60	17	2		6				
$DO(CH_2)_3OD$[b])		10		60	17		13					
$HOCD_2(CH_2)_2CD_2OH$		16		46	15	4			5		14	
$HOCH_2(CD_2)_2CH_2OH$	15			58	16	2		3				6
$HO(CH_2)_3(CD_2)_2(CH_2)_3OH$	42	21	14	14				5		4		

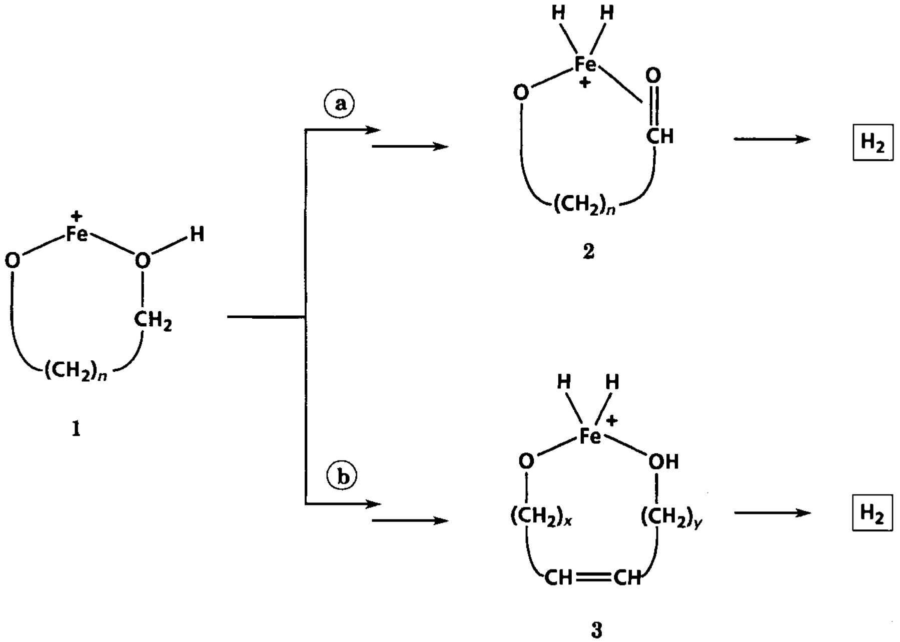
[a]) See *Footnote a* of *Table 1*.

[b]) For this precursor, the $[FeO(CH_2)_3OD]^+$ complex was mass-selected and its MI spectrum recorded.

This conjecture is indeed corroborated by the data of some isotopomers of several diols $HO(CH_2)_nOH$ (*Table 2*). For $n = 3$ and 4, the data reveal a highly site-specific process in the course of which the OH group is oxidized to a C=O function. In view of the previously demonstrated [4] propensity of Fe/diol complexes to form chelates, we suggest that the terminal aldehyde group formed in the dehydrogenation of $[FeO(CH_2)_nOH]^+$ undergoes intramolecular complexation of the metal ion (*Scheme;* path ⓐ). We note that the reaction **1** → **2** can also be viewed as a further example of the rare case of O–H bond activation by *late,* cationic transition-metal ions [7]. We presume that reaction ⓐ, shown in the *Scheme,* is also operative for the remaining homologues; however, with increasing chain length, in addition to oxidizing the OH group **1** → **2**, another mode of dehydrogenation becomes possible. This is evidenced by the data for $HO(CH_2)_3(CD_2)_2(CH_2)_3OH$. Here, in addition to H_2 loss, presumably *via* path ⓐ, we observe the elimination of HD and D_2. This clearly points to an activation of internal C–H/C–D bonds (path ⓑ), as was observed earlier for the $[Fe/HO(CH_2)_8OH]^+$ complex [4]. However, while the ratio of HD *vs.* D_2 loss corresponds to 1.5 for the $[FeO(CH_2)_3(CD_2)_2(CH_2)_3OH]^+$ system (*Table 2*), for the analogous $[Fe/HO(CH_2)_3(CD_2)_2(CH_2)_3OH]^+$ complex a ratio of 0.61 was observed [4]. Possibly, this is due to different directionalities operative in the 'unsymmetric' Fe^{II} alkoxides *vs.* the 'symmetric' Fe^I chelates.

The data in *Table 2* further reveal highly specific reactions for the losses of ethene and propene as well as formaldehyde. The olefin detachment involves C(1)–C(2) (for ethene) and C(1)–C(2)–C(3) (for propene), and formaldehyde involves an intact CH_2O group.

Scheme



However, on principal grounds the present data do not permit to distinguish the 'internal' $FeO(CH_2)_n$ moiety from the 'terminal' $(CH_2)_nOH$ group. In addition, the mechanistic details for the dehydration of Fe^{II} alkoxides remain unknown; as indicated by the labeling data, extensive exchange processes seem to precede the elimination.

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