Gas-Phase Ion Chemistry of Dimethyl Peroxide with the Bare Transition-Metal Cations Cr^+, Mn^+, Fe^+, and Co^+ †

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Abstract: Unimolecular and collision-induced fragmentations of dimethyl peroxide complexes $(CH_3OOCH_3)M^+$, with $M^+ = Cr^+$, Mn^+, Fe^+, and Co^+, were examined by means of tandem mass spectrometry and compared to results from bimolecular gas-phase reactions of the corresponding "bare" metal cations with dimethyl peroxide as studied by Fourier transform ion cyclotron resonance (FT-ICR) experiments. Bismethoxide metal ions, $(CH_3O)_2M^+$, are generated in the initial reaction step by insertion of the metal cation into the weak O−O bond of the peroxide. In the ion-beam apparatus these intermediates undergo a variety of processes involving β-H shifts, intramolecular redox reactions, and radical losses, depending on the respective metal cations. In contrast, the insertion products $(CH_3O)_2M^+$ formed in the ion/molecule reactions of dimethyl peroxide with bare metal cations in the FT-ICR mass spectrometer decompose to complexes $M(OCH_3)^+$ with concomitant loss of a methoxy radical, a process which is not observed in the unimolecular dissociation of metastable $(CH_3OOCH_3)M^+$ ions. The distinct differences between the unimolecular chemistry of dimethyl peroxide/M^+ complexes in the ion-beam apparatus and the bimolecular reactions of M^+ with dimethyl peroxide in the FT-ICR are explained in terms of internal energy effects, which result from the method of ion formation. This analysis is further supported by ligand-exchange reactions and collisional-activation experiments. In addition, analogies and differences of the gas-phase chemistry of dimethyl peroxide with M^+ as compared to metal-catalyzed decomposition of dialkyl peroxides in the condensed phase are discussed.

Introduction

Transition-metal-catalyzed oxidation of organic substrates constitutes one of the fundamental transformations in various branches of chemistry and biology.[1] In particular, the functionalization of saturated hydrocarbons into more valuable products is of large economic interest. Nevertheless, due to complicating bulk effects the mechanistic aspects of large-scale oxidation processes are often not very well understood if not completely unknown as far as elementary steps are concerned. Gas-phase studies turned out to be quite useful to provide further insight into the mechanisms of these processes, and within the last two decades the gas-phase chemistry of a broad variety of organic compounds with "bare" or partially ligated transition-metal cations has been probed by mass-spectrometric means.[2] As amply demonstrated, these experiments provide information on the intrinsic properties and reactivities of organometallic compounds, and it is hoped that these efforts will help to predict reactivity patterns for applied transition-metal catalysis in condensed-phase processes.

Surprisingly enough, the gas-phase chemistry of metal cations with peroxides has been almost completely neglected so far.[3,4] This is in contrast with the obvious importance of peroxo compounds in chemical and biological systems, e.g., as key intermediates in prostaglandin biosynthesis,[5] as well as in technical processes in which peroxides are widely used as radical sources,[6] e.g., in polymerization reactions or in the Hock process.[7] In addition, peroxides are valuable tools in organic chemistry not the least due to the synthetic power of peroxo compounds in metal-catalyzed oxidation reactions,[8] e.g., the Sharpless epoxidation.[8a]

Therefore, a systematic mass spectrometric study of the metal-induced chemistry of peroxo compounds is indicated in the hope to unravel mechanistic details of metal-mediated peroxide activation and oxygen atom transfer processes. In a recent investigation,[9] we screened the bimolecular gas-phase reactions of dimethyl peroxide (**1**; Chart 1) with most of the 3d, 4d, and 5d transition-metal cations. Basically, four reaction pathways

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† Dedicated to Professor A. Rieche, Berlin, a pioneer in the chemistry of organic peroxo compounds.

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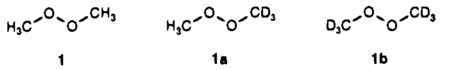
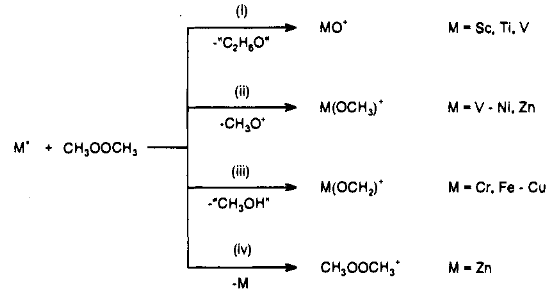
Chart 1



Scheme 1



have been observed, which are depicted in Scheme 1 for the 3d series. In the present paper we describe the results of an in-depth investigation on the reaction mechanisms of the first-row transition-metal cations Cr^+, Mn^+, Fe^+, and Co^+ with dimethyl peroxide (**1**) and its isotopologues **1a** and **1b** (Chart 1). This is accomplished by a combination of tandem and Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry.

Experimental Section

The experiments were performed by using a modified VG ZAB/HF/AMD four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sectors) and a Spectrospin CMS 47X FT-ICR instrument; both instruments have been described in detail previously.[10-12] Briefly, in the four-sector apparatus mixtures of dimethyl peroxide and $Cr(CO)_6$, $Mn_2(CO)_{10}$, $Fe(CO)_5$, and $Co(CO)_3(NO)$, respectively, were ionized by a beam of electrons having 50−100 eV kinetic energy in a chemical ionization source (CI; repeller voltage ca. 0 V).[13] The ions were accelerated to 8 keV translational energy and mass-selected by means of B(1)/E(1) at a resolution of $m/\Delta m$ = 2000−5000. Unimolecular fragmentations of metastable ions (MI) occurring in the field-free region preceding B(2) were recorded by scanning this sector. For collisional activation (CA) experiments ions were collided with helium (80% transmission). The errors of the relative intensities in MS/MS experiments do not exceed ±5%. MS/MS/MS experiments[14] were performed by selecting the parent ion with B(1)/E(1) and the daughter ions by means of B(2). The collision-induced fragmentations occurring in the field-free region between B(2) and E(2) were monitored by scanning E(2). The so-obtained spectra will be referred to as MI/CA and CA/CA spectra, respectively. On principal grounds, the ion currents in MS/MS/MS experiments are much smaller as compared to the MS/MS experiments; consequently, the error is estimated to ±20%. All spectra were accumulated and on-line processed with the AMD-Intectra data system; 5−30 scans were averaged to improve the signal-to-noise-ratio. Due to the relatively high pressure that prevails in the CI source, efficient collisional cooling of the ions takes place, such that excited states of M^+ ions are not likely to participate in the reactions observed.[2a,12,15]

In the FT-ICR experiments, M^+ ions were generated *via* laser desorption/laser ionization[16] in the external ion source by focusing the beam of a Nd:YAG laser (1064 nm) onto a pure metal target. The cations were extracted from the source by a system of electric potentials and lenses and transferred to the analyzer cell, where they were stored within the field of a superconducting magnet (Oxford Instruments, 7.05 T). The isolation of the most abundant isotope of the corresponding metal and all subsequent isolation steps were performed by using FERETS,[17] a computer-controlled ion-ejection protocol which combines single-frequency ejection pulses with frequency sweeps to optimize ion isolation. After isolation, the ions of interest were thermalized by collisions with pulsed-in argon gas and subsequently reisolated. Thermalization was assumed to be complete when no further change in reactivity occurred upon increasing the number of unreactive collisions.[18] Ligated metal cations $M(L)^+$ were generated by reacting bare M^+ cations with appropriate pulsed-in reagent gases as described elsewhere.[2,19] Dimethyl peroxide was subjected to multiple freeze−pump−thaw cycles and admitted to the FT-ICR cell *via* a leak valve at a pressure of ca. 10^{-8} mbar. High-resolution, double-resonance (DR), and collision-induced dissociation (CID) experiments were performed as described earlier.[11,20] All functions of the FT-ICR instrument were controlled by a Bruker Aspect 3000 minicomputer.

1 and **1b** (Chart 1) were synthesized[21] by alkylation of dihydrogen peroxide under basic conditions with dimethyl sulfate-d_0 and -d_6, respectively, purified by distillation, and characterized by their EI mass spectra.[22] Since the synthesis of isotopically pure **1a** is not straightforward, this compound was synthesized using a 1:1 mixture of dimethyl sulfate-d_0 and -d_6, resulting in a ca. 1:2:1 ratio of **1**, **1a**, and **1b**, and "isolation" of the requested isotopologue **1a** was realized *in situ* by means of tandem mass spectrometry. *Note that dimethyl peroxide is a hazardous substance and should be handled with appropriate precautions.*[23] Unfortunately, it became apparent during our initial studies that in commercial mass-spectrometric inlet systems significant thermal decomposition of the peroxides occurs. To alleviate this problem, we constructed a metal-free Teflon/glass inlet system for the four-sector instrument in which decomposition of peroxides is negligible; details of the design are available upon request.

Results and Discussion

The paper is organized such that we will first describe the unimolecular reactions of dimethyl peroxide/M^+ complexes as probed by tandem mass spectrometry, followed by a discussion of the bimolecular processes occurring under FT-ICR conditions when bare M^+ is reacted with **1**. Then, we will analyze the strikingly different results obtained in the two approaches and trace them back to effects of the internal energy content of **1**/M^+ that are caused by the method of ion formation. Finally, the implication of the gas-phase results for the metal-catalyzed decomposition of dialkyl peroxides in the condensed phase will be briefly discussed.

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Table 1. Mass Differences (amu) Observed in the Unimolecular Fragmentations of Metastable **1**/M$^+$ and its Isotopologues[a]

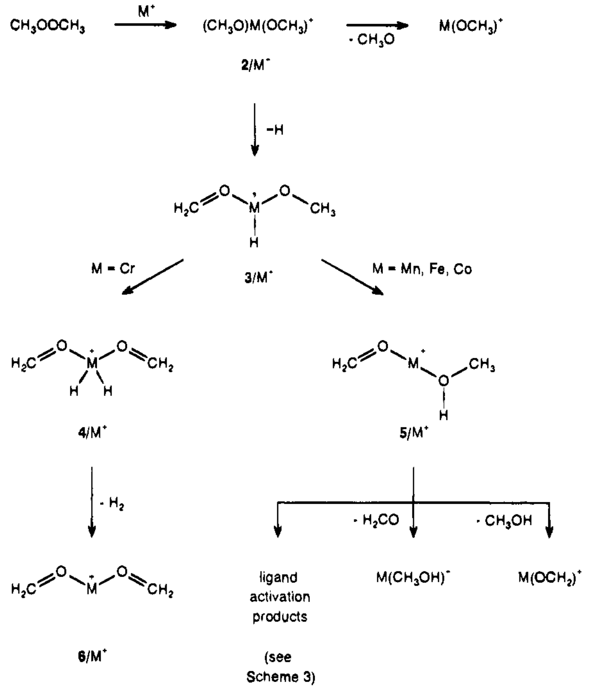
	$\Delta m =$														
	−1	−2	−3	−4	−15	−18	−20	−30	−31	−32	−33	−34	−35	−36	M$^+$
1/Cr$^+$		90						8		2					
1a/Cr$^+$		4	88	1				4		2	<1[b]		<1[b]		
1b/Cr$^+$				95						3				2	
1/Mn$^+$	3				4			83	2	5					3
1a/Mn$^+$	2	1			1	2		68	2	15	2	<1[b]	3		3
1b/Mn$^+$		2				3				87		1		4	3
1/Fe$^+$		2			59	35		3	1						
1a/Fe$^+$		4		<1[b]	9	76	4	3	1	1					
1b/Fe$^+$				2		60	33			4		1			
1/Co$^+$		75						17		8					
1a/Co$^+$		61	2	16				12		3	1		5		
1b/Co$^+$				57						39				4	

[a] Intensities are normalized to Σ(reactions) = 100%. [b] For the sake of clarity, intensities of less than 1% are usually omitted.

Before doing so, we would like to point out that the weak O—O bond of peroxides facilitates the insertion of a metal cation into this bond, leading to $(CH_3O)_2M^+$; these intermediates exhibit a chemistry which depends extremely on both the internal energy of the insertion product and the electronic properties of the metal. The insertion reaction itself is estimated to be exothermic by more than 100 kcal/mol.[24]

Unimolecular Fragmentation of 1/M$^+$. Table 1 sums up the intensities of unimolecular fragmentation reactions of **1**/M$^+$ cations (M = Cr, Mn, Fe, and Co), which can be classified as follows: (i) Cr$^+$ leads preferentially to a $(CH_2O)_2Cr^+$ complex **6**/Cr$^+$; as will be demonstrated in detail this bisformaldehyde complex results from two consecutive β-H shifts from either methoxide ligand to the metal center followed by reductive elimination of molecular hydrogen. Formally, this process corresponds to an oxidation of the dimethyl peroxide ligand. (ii) The formation of $(CH_3OH)(CH_2O)M^+$ complexes **5**/M$^+$ represents the key step in the reactions of the metal cations Mn$^+$, Fe$^+$, and Co$^+$ and can be classified as a metal-mediated intramolecular redox reaction of the peroxide. Intermediate **5**/M$^+$ may decompose by either simple detachment of formaldehyde or methanol or activation of the ligand(s); depending on the metal ion in the latter process, closed (H_2, H_2O) and open shell ($H^\bullet$, $CH_3^\bullet$, $CH_3O^\bullet$) neutrals will be eliminated. Methoxy loss may also proceed directly from **2**/M$^+$ (Scheme 2).

Scheme 2



As already mentioned, the major fragmentation process of **1**/Cr$^+$ corresponds to the loss of molecular hydrogen (Δm = 2), and upon deuteration of one methyl group mainly HD loss (Δm = 3 for **1a**/Cr$^+$) is observed (Table 1). Assuming a $(CH_3O)_2Cr^+$ complex (**2**/Cr$^+$) as the first intermediate, two subsequent β-H transfer steps (**2**/Cr$^+$ → **3**/Cr$^+$ → **4**/Cr$^+$) lead to the formation of **4**/Cr$^+$ which eventually eliminates H_2 (HD from **1a**/Cr$^+$, and D_2 from **1b**/Cr$^+$). Similar β-H shifts within methoxide/M$^+$ complexes have been observed in the reactions of nitromethane[26] with M$^+$ (M = Fe, Co, Ni, Cu, Rh, Pd, Ag); for the *tert*-butoxide/Fe$^+$ system even a rather unusual β-methanide shift has been reported.[27] However, the $(CH_3O)_2Cr^+$ complex constitutes the first example for consecutive β-hydrogen shifts from two separate methoxy ligands attached to a transition-metal center. The assignment of a $(CH_2O)_2/Cr^+$ structure (**6**/Cr$^+$) as the product ion arising from the dehydrogenation of **1**/Cr$^+$ is supported by their collisional activated decomposition pattern: The MI/CA spectrum of **6**/Cr$^+$ exhibits only one major process, i.e., the detachment of a CH_2O ligand. Similarly, for **6a**/Cr$^+$ two major products are observed in a ca. 1:1 ratio, i.e., losses of formaldehyde (Δm = 30) and formaldehyde-d_2 (Δm = 32). All other reactions found in the MI/CA spectra are much less abundant and can be attributed to either consecutive ligand loss or metal-induced activation of the ligands.[28] The proposed mechanism (Scheme 2) also accounts for the two minor peaks at Δm = 30 and Δm = 32 in the MI spectrum of **1**/Cr$^+$, which correspond to the loss of formaldehyde

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(24) For example, an exothermicity of 121 kcal/mol for the formation of $(CH_3O)_2Fe^+$ can be extracted from literature data (ref 25) assuming BDE-(Fe$^+$−OH) ≅ BDE(Fe$^+$−OCH$_3$) and using a simple additivity scheme as described in Benson, S. W. *Thermodynamical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*, 2nd ed.; Wiley: New York, 1976. ΔH_r (**2**/Fe$^+$) ≅ BDE(RO−OR) − 2BDE(M−OH$^+$) = BDE(RO−OR) − $2[\Delta H_f(M^+) + \Delta H_f(OH) - \Delta H_f(MOH^+)]$.

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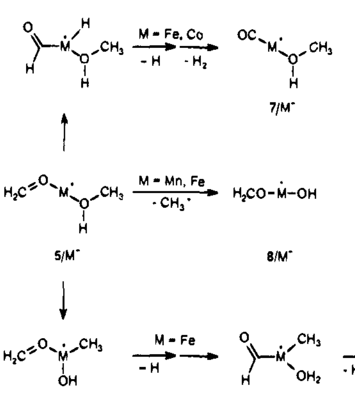
Scheme 3



and the reductive elimination of methanol from **3**/Cr$^+$ *via* **5**/Cr$^+$, respectively; consecutive losses of H_2 and CH_2O (or vice versa) may also contribute to the $\Delta m = 32$ mass difference. It should be mentioned that the minor contributions of H_2 and D_2 ($\Delta m =$ 2 and 4) in the dehydrogenation of **1a**/Cr$^+$ as well as the absence of signals due to the losses of formaldehyde-d_1 and methanol-d_2 point to the existence of another reaction path which cannot be explained in terms of H/D exchange processes between the methoxy groups. Rather an alternative pathway must exist, and as will be shown below, it is this alternative pathway which dominates the metastable ion decomposition of **1**/Co$^+$.

At first sight the MI data of **1**/Co$^+$ do not seem to exhibit very pronounced differences as compared to **1**/Cr$^+$, in that dehydrogenation dominates for both complexes while formaldehyde and methanol are formed as side products. However, the isotopologous complex **1a**/Co$^+$ eliminates only small amounts of HD (2%), while formations of H_2 and D_2 are by far more intense (61% and 16%, respectively). This finding clearly points to the operation of a genuine 1,1-dehydrogenation of a methoxy group by cationic Co$^+$.[29] A possible reaction sequence (Schemes 2 and 3) may proceed *via* **5**/Co$^+$ to generate **7**/Co$^+$, whose $(CH_3OH)(CO)Co^+$ structure is supported by the MI/CA spectra of **7**/Co$^+$ and its isotopologues: The loss of carbon monoxide ($\Delta m = 28$) is the dominant process in the collisional activation experiment accompanied by a less abundant expulsion of methanol and regeneration of Co$^+$. Of course, the intermediate **5**/Co$^+$ can also act as a precursor en route to the coupled losses of formaldehyde ($\Delta m = 30$) and methanol ($\Delta m = 32$). The assumption of **5**/Co$^+$ as an intermediate is substantiated by the MI and CA spectra of $(CH_3OH)(CH_2O)Co^+$, independently generated by chemical ionization of a mixture of methanol, formaldehyde, and $Co(CO)_3(NO)$; these spectra are practically identical to those obtained from **1**/M$^+$. The mechanistic scenario proposed for the Co$^+$ complex of **1** is in good agreement with the observed deuterium distribution in the MI spectra of **1a**/Co$^+$: In addition to the preferred eliminations of H_2 and D_2 (see above), one expects losses of formaldehyde (Δm $= 30$), formaldehyde-d_2 ($\Delta m = 32$) methanol-d_1 ($\Delta m = 33$), and methanol-d_3 ($\Delta m = 35$), respectively, depending on the methyl group from which the H or D atom is initially transferred. These products are indeed observed experimentally; moreover, the ca. 4:1 ratio for H_2:D_2 eliminations is also found for the products $CH_2{=}O$:$CD_2{=}O$ and CD_3OH:CH_3OD. Thus, we conclude that (i) **5**/Co$^+$ serves as a common precursor for ligand detachment as well as for dehydrogenation and (ii) the H(D) transfer **2**/Co$^+$ → **5**/Co$^+$ constitutes the rate-determining step (RDS) with a kinetic isotope effect (KIE) of ca. $k_H/k_D = 4$. Once **5**/Co$^+$ is formed, it gives rise to the observed product distribution without any significant barrier. The apparent inverse KIE as manifested in the preferential CD_3OH loss can be interpreted as a logical consequence of a preceding hydrogen atom transfer step; in contrast, for the formation of CH_3OD transfer of a deuterium atom has to take place (see below).

For the Fe$^+$ complex of **1** we assume that the formal disproportionation complex **5**/Fe$^+$ once more serves as a central intermediate. This is indicated by the losses of H_2 and D_2 from **1a**/Fe$^+$ and further supported by the MI and CA spectra of independently generated **5**/Fe$^+$; these spectra are identical within experimental error to those obtained from **1**/Fe$^+$. However, in contrast to **1**/Co$^+$, the major fragmentation processes of **1**/Fe$^+$ are due to losses of a methyl radical and of water (Table 1). The connectivities (Scheme 3) of the resulting product ions, i.e., [**1**/Fe$^+$ − $CH_3^•$] and [**1**/Fe$^+$ − H_2O], have been deduced from the respective MI/CA and CA/CA spectra. In addition, CA spectra of the ions extracted directly from the ion source have been recorded. For each process the CA and the MI/CA or CA/CA spectra are in fairly good agreement with each other (Tables 2 and 3).[30] As shown in Table 2, collisionally activated [**1**/Fe$^+$ − $CH_3^•$] ions exhibit two major processes. These correspond to the losses of an OH radical ($\Delta m = 17$) and of an intact formaldehyde ligand ($\Delta m = 30$). Both reactions are in keeping with structure **8**/Fe$^+$ for the [**1**/Fe$^+$ − $CH_3^•$] ion (Scheme 3). For the product ion corresponding to H_2O loss from **1**/Fe$^+$, the CA spectrum of [**1**/Fe$^+$ − H_2O] and that of independently generated acetaldehyde/Fe$^+$ nicely match each other;[31] therefore, we assign structure **9**/Fe$^+$ to the [**1**/Fe$^+$ − H_2O] ion. If the reaction sequences depicted in Scheme 3 are correct, from **1a**/Fe$^+$ one expects losses of $CH_3^•$ ($\Delta m = 15$), $CD_3^•$, and its isobaric H_2O ($\Delta m = 18$), as well as D_2O ($\Delta m =$ 20), but no H/D equilibrated products like $CH_{3-x}D_x$ or HDO. This is indeed born out in the experiment (Table 1). As already discussed for the Co$^+$ complexes, a rate-determining hydrogen transfer process, **2**/Fe$^+$ → **3**/Fe$^+$, should result in a normal KIE for the water loss (i.e., $k(H_2O)/k(D_2O) > 1$) and a seemingly inverse KIE for the methyl loss ($k(CH_3)/k(CD_3) < 1$).[32,33] Due to the low intensities of the dehydrogenation products from **1a**/Fe$^+$ (Table 1), the KIE of the H transfer cannot be derived precisely from the H_2:D_2 ratio. However, a KIE of ca. 6 seems to be a good estimate, since this number reproduces quite satisfactorily the observed $CH_3^•$:($CD_3^•$ + H_2O):D_2O ratio of 9:76:4 (Scheme 4): Namely, if we assume that the step **2**/Fe$^+$ → **5**/Fe$^+$ is indeed rate-determining, one predicts a $CH_3^•$:$CD_3^•$ ratio of 9:54 and a H_2O:D_2O ratio of 24:4, resulting in an overall 9:78:4 ratio of $CH_3^•$:($CD_3^•$ + H_2O):D_2O: This prediction is in excellent agreement with the experimental result. The assumption of a rate-determining hydrogen atom transfer is further supported by the MI spectrum of **1b**/Fe$^+$ which is practically identical to that of **1**/Fe$^+$ as far as the relative intensities of the product ions are concerned. Obviously, intermolecular kinetic isotope effects in the reactions of **1**/Fe$^+$ and **1b**/Fe$^+$ are of minor importance if they exist at all. This finding rules out the possibility of two (or more) competing reaction pathways subject to different KIEs. For such a situation one would normally

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(29) For another example of a metal-induced 1,1-dehydrogenation of a methoxy group and leading references, see: Prüsse, T.; Fiedler, A.; Schwarz, H. *J. Am. Chem. Soc.* **1991**, *113*, 8335.

(30) The minor differences in the intensities of CA, MI/CA, or CA/CA spectra can be attributed to different internal energies.

(31) Also see: Fiedler, A. Diploma Thesis, Technische Universität Berlin, 1992. In this work 10 different $[Fe,C_2,H_4,O]^+$ isomers were generated and distinguished by means of their CA spectra.

(32) The "inverse" KIE for the methyl loss strongly indicates that a simple C−O bond cleavage process, followed by a H transfer, can be excluded. Instead, the inverse isotope effect is the result of a hidden hydrogen rearrangement in which it is the primary KIE that matters in the multistep event. For a further analysis and many examples, see ref 33.

(33) Schwarz, H. *Top. Curr. Chem.* **1981**, *97*, 1.

Table 2. CA, MI/CA, and CA/CA Spectral Data of $[Fe,C,H_3,O_2]^+$ Ions[a]

assigned ion structure		$HOFe(CO)^+$	$HOFeO^+$	$Fe(CH_2O)^+$	$Fe(CO)^+$	$FeOH^+$	FeO^+	FeH^+	Fe^+
neutral lost		H_2	CH_2	OH	$H_2 + OH$	CH_2O	$[CH_3O]$	$[CH_2O_2]$	$CH_2O + OH$
[**1**/Fe$^+$ − CH$_3$]	CA[b]	9	3	38	8	100	8	2	21
[**1**/Fe$^+$ − CH$_3$]	MI/CA[b]	11	5	65	12	100	10	4	12
[**1**/Fe$^+$ − CH$_3$]	CA/CA[b]	12	6	45	10	100	7	4	22

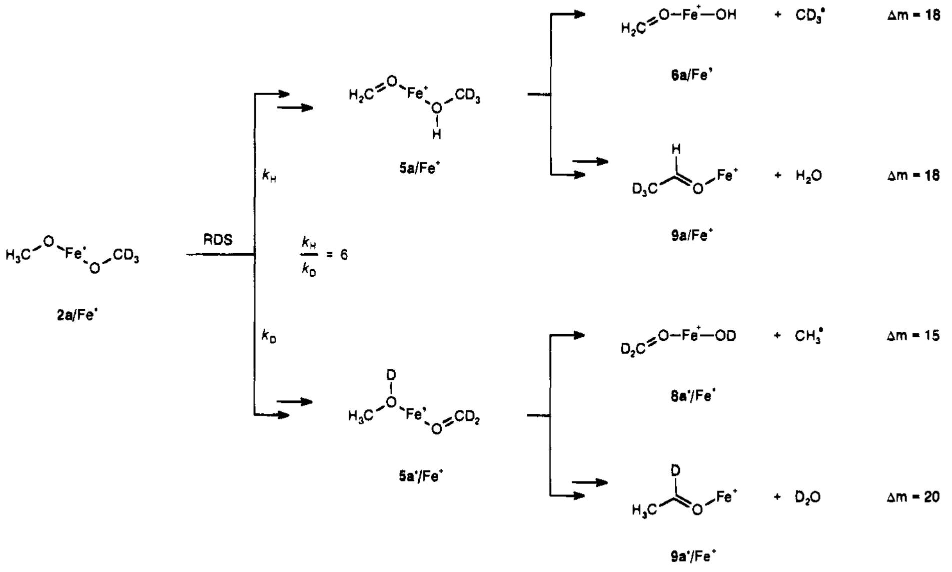
[a] Intensities are given relative to the base peak (100%). For the sake of brevity, side reactions are omitted. [b] CA spectrum of $[Fe,C,H_3,O_2]^+$ ions generated from a mixture of dimethyl peroxide and $Fe(CO)_5$ and directly extracted from the ion source. MI/CA and CA/CA are CA spectra of $[Fe,C,H_3,O_2]^+$ fragments generated by metastable and collisionally activated decompositions of **1**/Fe$^+$.

Table 3. CA, MI/CA, and CA/CA Spectral Data of $[Fe,C_2,H_4,O]^+$ Ions[a]

assigned ion structure		$FeCO^+$	$FeOH^+$	$HFeCH_3^+$	$FeCH_3^+$	$FeCH_2^+$	$FeCH^+$	FeH^+	Fe^+	CH_3CO^+
neutral lost		CH_4	$[C_2H_3]$	CO	HCO	CH_2O	CH_3O	$[C_2H_2O]$	CH_3CHO	FeH
$[FeCH_3CHO^+]$	CA[b]	16	2	11	8	1	1	12	100	1
[**1**/Fe$^+$ − H$_2$O]	CA[c]	22	5	10	10	2	2	14	100	<1
[**1**/Fe$^+$ − H$_2$O]	MI/CA[c]	25	2	17	14	1	4	17	100	1
[**1**/Fe$^+$ − H$_2$O]	CA/CA[c]	29	3	12	11	2	5	13	100	2

[a] Intensities are given relative to the base peak (100%). For the sake of brevity, side reactions are omitted. [b] See ref 31. Ions generated from $Fe(CO)_5$ and acetaldehyde. [c] CA spectrum of $[Fe,C_2,H_4,O]^+$ ions generated from a mixture of dimethyl peroxide and $Fe(CO)_5$ and directly extracted from the ion source. MI/CA and CA/CA are CA spectra of $[Fe,C_2,H_4,O]^+$ fragments generated by metastable and collisionally activated decompositions of **1**/Fe$^+$.

Scheme 4



expect the operation of isotopically sensitive branching, thus resulting in quite different intensity distributions in the MI spectra of the unlabeled and the labeled isotopomers as well as of opening up new reaction channels.[34,35] In conclusion, the inverse KIE for $CH_3^•$ versus $CD_3^•$ loss can be traced back to a rate-determining hydrogen transfer step which precedes dissociation; this phenomenon is quite common in organic mass spectrometry and has previously been analyzed in terms of "hidden hydrogen rearrangements".[33]

The consecutive reactions of **5**/M$^+$ are another example of ligand effects on the metal-mediated bond activation of methanol (Scheme 2): While no exothermic reaction channel is accessible for the reaction of bare Fe$^+$ with methanol,[36] a few examples of O—H bond activation have been reported for complexes containing suitable ligands L: The methanol/$FeCH_3^+$ system, for example, liberates methane *via* oxidative addition of the O—H bond to the metal center (Scheme 5).[37] Similarly, Fe(butadiene)$^+$ leads to RO—H bond activation of alcohols.[38] These findings emphasize that not only the properties of M$^+$ but also the nature of the ligand L determines the reactivity as well as the site of bond activation in methanol/M(L)$^+$ complexes. More precisely, ligands which are good hydrogen atom acceptors (e.g., a methyl group or butadiene) lead to O—H bond activation of methanol, while the formaldehyde ligand in **5**/Fe$^+$ serves as a hydrogen donor, thus promoting the C—O bond activation of methanol and resulting in the formation of **9**/Fe$^+$ and water (Scheme 5).

Finally, we will briefly refer to **1**/Mn$^+$, for which the major

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(34) The MI spectra of the Co$^+$ system of **1** and its isotopologues may serve as an example. Here, the signal intensities of the MI spectra of **1**/Co$^+$ differ indeed from those observed for **1b**/Co$^+$. For example, the loss of HD from **1a**/Co$^+$ points to a slight contribution of an independent dehydrogenation mechanism. Thus, two reactions compete with each other, and consequently isotopically sensitive branching (see ref 35) may be the origin for the observed differences between **1**/Co$^+$ and **1b**/Co$^+$. However, these arguments do not apply for the Fe$^+$ complexes, since there is no HD loss from **1a**/Fe$^+$ at the detection limit of the instrument.

(35) Thibblin, A.; Ahlberg, P. *Chem. Soc. Rev.* **1989**, *18*, 209.

(36) (a) Huang, S.; Holman, R. W.; Gross, M. L. *Organometallics* **1986**, *5*, 1856. (b) Prüsse, T., Ph.D. Thesis, Technische Universität Berlin D83, 1992. (c) Also, see: Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998.

(37) Blum, O.; Stöckigt, D.; Schröder, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 603 and references cited therein.

(38) Karrass, S.; Schröder, D.; Schwarz, H. *Chem. Ber.* **1992**, *125*, 751.

Scheme 5

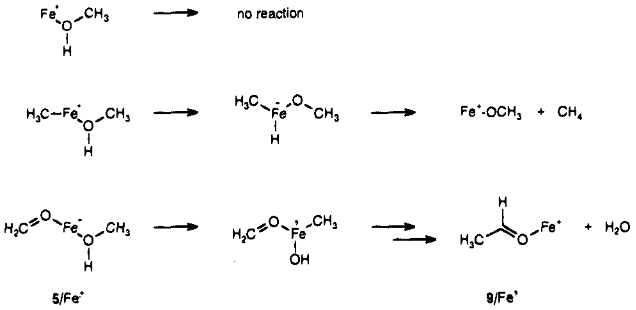


Table 4. Ionic Products of the Ion/Molecule Reactions of Bare M^+ with Dimethyl Peroxide in the FT-ICR[a]

	Cr^+	Mn^+	Fe^+	Co^+
$(CH_2O)M^+$	34		7	25
$(CH_3O)M^+$	66	100	93	75

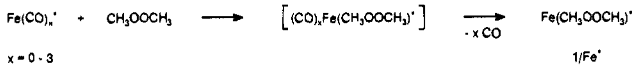
[a] Intensities are normalized to Σ(reactions) = 100%.

fragmentation process corresponds to the loss of formaldehyde (Table 1); interestingly, elimination of CH_3OH is much less pronounced. In analogy to the reactions of the **1**/Fe^+ and **1**/Co^+ complexes, we assume that also for the Mn^+ system the intermediate **5**/M^+ serves as a precursor for the formations of CH_2O and CH_3OH. In addition, consecutive losses of methanol and formaldehyde take place to regenerate bare Mn^+ ions; minor radical losses are also observed, i.e., $H^•$ (Δm = 1), $CH_3^•$ (Δm = 15), and $CH_3O^•$ (Δm = 31). The data of the labeled compounds are in keeping with this interpretation. The unimolecular formation of radicals may reflect the $4s^13d^5$ electron configuration of Mn^+, which promotes the formation of one covalent bond to an open shell ligand *via* the 4s orbital. We note that for Fe^+ with its $4s^13d^6$ ground state the loss of an open shell neutral (i.e., the methyl loss from **5**/Fe^+) represents the major reaction channel.

Ion/Molecule Reactions of 1 with Bare M^+. Quite a different product distribution is observed when bare M^+ is reacted with **1** under FT-ICR conditions (Table 4).[9] For M = Cr, Mn, Fe, and Co the formation of metal alkoxide cations by and large dominates, and the generation of $(CH_2O)M^+$ is less pronounced if not absent; no other rearrangement products are observed. In addition, for **1a** and **1b** no significant KIEs become apparent. Although one cannot a priori expect that unimolecular fragmentation in an ion-beam instrument resembles the branching ratio produced in a bimolecular FT-ICR experiment, drastic changes in reactivity as expressed by the data shown in Tables 1 and 4 have not been reported previously. For example, the ICR and MI reactivity of RCN/Fe^+ complexes is by and large comparable.[12] In contrast, in the unimolecular dissociation of **1**/Fe^+, products due to rearrangement (i.e., $CH_3^•$ and H_2O) amount to 94%, while these species are not observed at all in the ion/molecule reaction of bare Fe^+ with **1**.

Internal Energy Effects. The bimolecular gas-phase chemistry of a few organometallic systems in FT-ICR experiments has earlier been compared to unimolecular decompositions of the corresponding substrate/M^+ complexes studied by tandem mass spectrometry.[12,19b] Despite some differences in product abundances these studies revealed that the reactivity in terms of reaction channels is comparable for both experimental methods. In distinct contrast, the dimethyl peroxide/M^+ system exhibits a totally different behavior. As will be shown below, this observation can be traced back to the internal energy of the reactive species. The internal energy content is determined by an interplay of the highly exothermic initial insertion step **1**/M^+ → **2**/M^+ and the experimental conditions, in particular collisional cooling efficiency in the formation of **1**/M^+.

Scheme 6



In the FT-ICR mass spectrometer thermalized metal cations undergo a bimolecular collision with dimethyl peroxide to form a short-lived encounter complex, which immediately reacts *via* metal insertion into the O−O bond, yielding a $(CH_3O)_2M^+$ structure. The so-formed **2**/M^+ is rovibrationally excited by more than 100 kcal/mol (see above),[24] and energy transfer to other molecules is ineffective due to the low collision rate at a pressure of ca. 10^{-8} mbar prevailing in the FT-ICR cell. Thus, it is quite clear that sufficient energy is available for the simple cleavage of an M^+−OCH_3 bond (e.g., BDE(Fe−OH^+) ≅ 79 kcal/mol)[12] leading to the metal alkoxide cations $(CH_3O)M^+$ and a methoxy radical. These products do indeed correspond to the main reaction in the FT-ICR (Table 4) and can be taken as a diagnostic for the bimolecular reaction of bare metal cations with dimethyl peroxide. This "high-energy process" is to be distinguished from the "low-energy" rearrangement reaction, as for example the formation of $(CH_2O)M^+$;[39] this product most likely is due to the expulsion of methanol after the rearrangement **2**/M^+ → **5**/M^+.

In contrast, in the CI source of the ion-beam apparatus the dimethyl peroxide/M^+ complexes are formed *via* substitution processes as depicted in Scheme 6 for the chemical ionization of a mixture of **1** with $Fe(CO)_5$. For example, not only complexation of **1** by bare Fe^+ ions and subsequent collisional stabilization of the adducts contribute to the ion beam of **1**/Fe^+; rather **1**/Fe^+ is formed *via* ligand exchange reactions of $Fe(CO)_x^+$, such that evaporation of the CO ligand(s) removes part of the internal energy.[40] In addition, subsequent collisional stabilization in the ion source ($p \approx 10^{-3}$ mbar) provides effective cooling of the ions. Although chemical ionization leads to **1**/M^+ ions with a broad distribution of internal energy, highly excited ions are likely to decompose before they reach the field-free region preceding the second magnetic analyzer. As a consequence, in the unimolecular fragmentations of metastable **1**/M^+ occurring in this region, species with a relatively narrow energy window are sampled,[41] which lies rather below the energy of the [**1** + M^+] entrance channel as monitored under FT-ICR conditions. Therefore, in the MI spectra the cleavage of the $(CH_3O)M^+$−OCH_3 bonds of **2**/M^+ is hardly accessible and rearrangement processes dominate, resulting in the formation of thermochemically more stable products.

Two experiments have been conducted to probe this concept: (i) If dimethyl peroxide is reacted in the FT-ICR with partially ligated $M(L)^+$ ions, the internal energy should be better distributed within the rovibrationally excited **1**/$M(L)^{+*}$, since the additional ligand provides further degrees of freedom. Moreover, when the ligand L is detached from **1**/$M(L)^{+•}$ (or its isomer **2**/$M(L)^{+*}$) part of the internal energy is consumed in the cleavage of the ligand−metal bond; as a consequence, the internal energy content of the so-formed **2**/M^+ decreases and rearrangement processes are expected to start to compete with the cleavage of the M^+−OCH_3 bond of **2**/M^+. (ii) Vice versa,

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[39] Mn^+ does not form the $(CH_2O)Mn^+$ ion in the FT-ICR experiment. This can be ascribed to the high Mn−OR^+ bond dissociation energy and the $4s^13d^5$ ground state configuration of the manganese cation. For further details, see ref 9.

[40] Vertes, A.; Gijbels, R.; Adams, F. *Mass Spectrom. Rev.* **1990**, *9*, 71.

[41] Williams, D. H.; Howe, I. *Principles of Organic Mass Spectrometry*; McGraw-Hill: London, 1972.

Table 5. Products Generated by Bimolecular Reactions of $Fe(L)^+$ Complexes with Dimethyl Peroxide (**1**) (FT-ICR)[a]

ligand (L)	$(L)Fe(OCH_3)^+$	$(L)Fe(OH)^+$	$(L)Fe(H)^+$	$(CH_2O)Fe(OH)^+$	$Fe(HOCH_3)^+$	$Fe(OCH_2)^+$
ethene	22			16	43	19
propene	15			40	40	5
isobutene	35			35	30	
benzene	43		26	14	17	
acetone	30	70				

[a] Intensities are normalized to Σ(reactions) = 100%.

upon collisional activation of **1**/M^+ (or **2**/M^+) in the ion-beam instrument the internal energy of the ions increases such that the loss of a methoxy radical should also be observed.

In order to prove these energetic effects, the results obtained for the **1**/Fe^+ system may serve as an example. Table 5 summarizes the products of the ion/molecule reactions of $Fe(L)^+$ (L = alkenes, benzene, acetone) with dimethyl peroxide (**1**) in the FT-ICR mass spectrometer. The ionic reaction products containing the ligands L correspond to the loss of a methoxy radical from the inserted intermediate **2**/$Fe(L)^+$, yielding $(CH_3O)Fe(L)^+$; the benzene/FeH^+ ion can be attributed to consecutive methoxy radical and formaldehyde losses from the initial product $(CH_3O)_2Fe(C_6H_6)^+$. The acetone/$Fe(OH)^+$ complex originates from consecutive losses of formaldehyde and a methyl radical most probably involving a rearrangement to **5**/Fe(acetone)$^+$. In this complex acetone is bound more strongly as compared to formaldehyde, thus leading to the detachment of the latter rather than the acetone ligand. The other reaction products can be traced back to the elimination of $CH_3^\bullet$, CH_2O, and CH_3OH, respectively, following the evaporation of the ligand L.[19,42] The corresponding ionic products are also observed in the unimolecular dissociation of metastable **2**/Fe^+. Their formation can be accounted for by a decrease of the internal energy content of **2**/Fe^{+*}, when it is formed *via* a ligand exchange process from $Fe(L)^+$ as compared to the reaction of the bare metal ion itself. For example, while in the reaction of bare Fe^+ with **1** the formation of $(CH_3O)Fe^+$ predominates (93%), this product is not observed at all for the reaction with $Fe(L)^+$. This is because the internal energy content of **2**/Fe^{+*}, formed from **1** and $Fe(L)^+$ by replacement of L, is no longer sufficient for homolytic cleavage of a bond in the intermediate **2**/Fe^+; consequently, only less energy demanding rearrangement products evolve. Also not that for none of the ligands studied neither ligand coupling nor oxygen atom transfer from the peroxide to the ligand occurs. However, for L = acetone a formal hydroxide transfer is observed. Although this process is seemingly surprising in that OH transfer to the metal has not been observed in any other reaction, the formation of this product is easily explained by the fact that acetone is more strongly bound to a metal ion than formaldehyde. Thus, **5**/Fe(acetone)$^+$ is more likely to undergo consecutive losses of a methyl radical and formaldehyde rather than that of a methyl radical and acetone.

In a different experiment the internal energy content of **1**/M^+ has been affected by subjecting the mass-selected metastable ion complexes to collisional activation in the ion-beam instrument. As demonstrated by the data in Table 6, loss of $CH_3O^\bullet$ (Δm = 31), which is minor if not absent in the MI spectra (Table 1) and which dominates the FT-ICR experiment (Table 4), gains in importance upon collisional activation.

According to the classification given above, Figure 1 displays the relative amounts of "methoxy loss" versus "rearrangement products" for the **1**/Fe^+ system obtained under different experimental conditions. The ratio of both processes, although qualitative in nature, clearly reflects the effect of the internal energy of the ions sampled in these experiments. As noted above, we cannot distinguish between excited **1**/Fe^{+*} and **2**/Fe^{+*}, and therefore we will only refer to **2**/Fe^+ in the following discussion. On the basis of the data depicted in Figure 1, one can deduce a schematic potential energy diagram (Figure 2) for the reaction of **1** with Fe^+ and $Fe(L)^+$ at various energy contents.[19] The FT-ICR reaction of **1** with bare Fe^+ leads to highly excited **2**/Fe^+ complexes, possessing enough energy for the entropically favored cleavage of an M^+-OCH_3 bond, such that rearrangement processes can no longer compete efficiently.

Table 6. Collisional Activation Fragmentation Processes Observed for the Dimethyl Peroxide/M^+ Complexes[a]

	Δm =										
	−1	−2	−15	−18	−30	−31	−32	MOH^+	MO^+	MH^+	M^+
1/Cr^+		57	7		100	18	60	7	6	4	13
1/Mn^+	3		5		100	11	14	7	1	4	9
1/Fe^+	11	3	100	19	49	21	17	6	2	6	7
1/Co^+		20	9		100	13	84	9	2	4	16

[a] Intensities are given relative to the base peak (100%). For the sake of clarity, some minor processes are omitted.

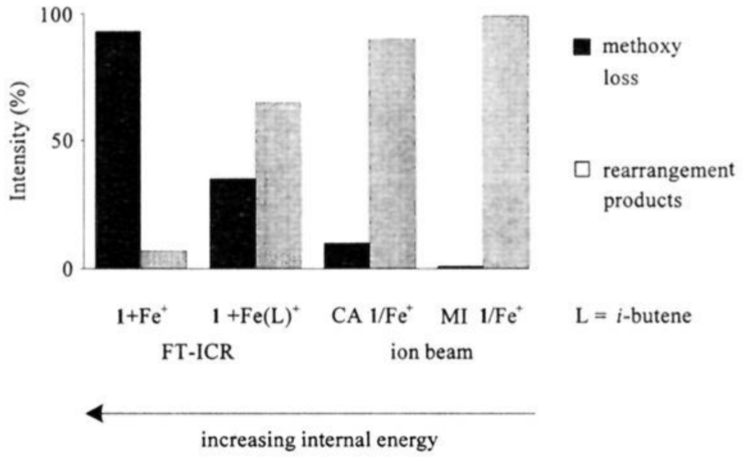

Figure 1. Relative amounts of methoxy loss and rearrangement products observed for the gas-phase reactions of **1** with M^+ using different experimental setups (see text).

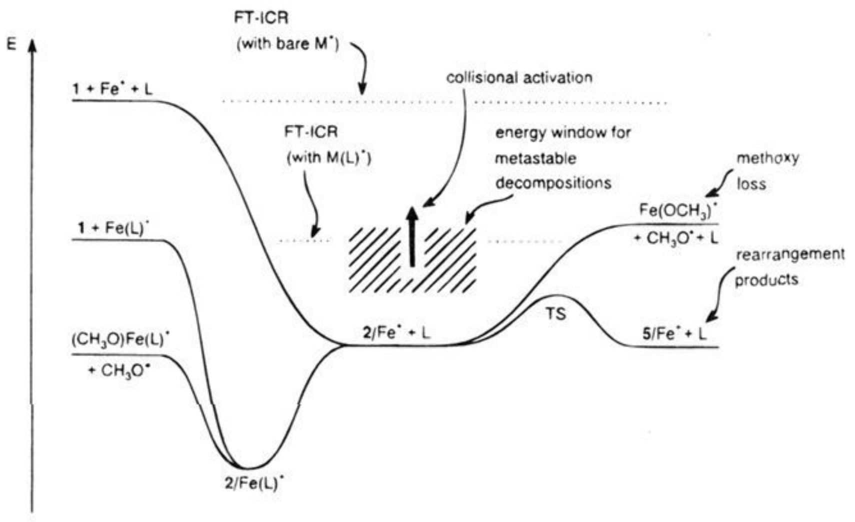

Figure 2. Schematic potential energy surface diagram for the gas-phase reaction of **1** with bare or ligated metal cations and qualitative energy windows which are sampled by the different experimental methods.

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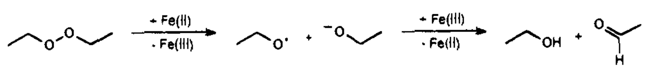
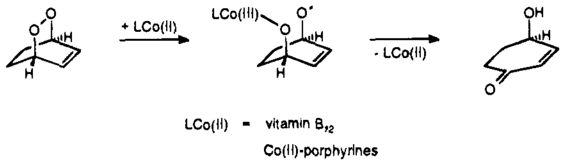
[42] Interestingly, water loss is not observed for **1**/$Fe(L)^+$. This seems to be due to the fact that the ratio of methyl and water losses is very sensitive to changes in internal energy: From the MI spectrum of **1**/Fe^+ a ratio of ca. 1.7:1 can be deduced, while the CA spectrum exhibits a ca. 5:1 ratio. Thus, we assume that upon further increase of internal energy the expulsion of methyl radicals will be largely favored at the expense of water formation.

Scheme 7



Scheme 8



In the reaction of **1** with $Fe(L)^+$ detachment of the ligand L leads to a **2**/Fe^{+*} complex which is less excited by the amount of the complexation energy of the ligand L; the so-formed intermediates undergo exclusively rearrangement reactions. Loss of a methoxy ligand is only accessible directly from **2**/$Fe(L)^+$ *prior* to detachment of L. Thus, the formation of $(CH_3O)Fe^+$ is negligible, while $(CH_3O)Fe(L)^+$ is formed to some extent for all ligands studied here. Similarly, upon collisional activation of metastable **2**/Fe^+ the methoxy loss becomes energetically accessible, while it is hardly observed in the MI spectrum of **2**/Fe^+, in which products due to rearrangement dominate. Therefore, we conclude that the energy window of this particular experiment is situated energetically below the thermochemical threshold of the methoxy loss from **2**/Fe^+. Consequently, the transition structure (TS) associated with the rearrangement process **2**/Fe^+ → **5**/Fe^+ exhibits a lower energy demand than the methoxy loss channel.

Comparison of Gas- and Condensed-Phase Chemistry. In the condensed phase the influence of metal cations on the decomposition of dialkyl peroxides was first studied in the early 1930s.[43] For example, ethanol and acetaldehyde were observed as products in the Fe(II)-catalyzed decomposition of diethyl peroxide.[43a] The mechanism proposed for this process (Scheme 7) involves the initial formation of free ethoxy radicals and a subsequent electron transfer to generate an ethoxide anion; this corresponds to an oxidation of the metal (Fe(II) → Fe(III)) and a reduction of the peroxide. Depending on the nature of the solvent, the ethoxide anions are complexed to the metal cation or exist as solvated species. Moreover, formation of alkoxy radicals from higher dialkyl peroxides is followed by a rich chemistry, depending on the conditions of the reaction and the substituents of the peroxide.[44] One possible reaction channel for the ethoxy radicals represents the abstraction of a hydrogen atom from the ethoxide, which then yields acetaldehyde and the reduced form of the catalyst, e.g., Fe(II). Similarly, endoperoxides (Scheme 8) can be rearranged—even stereoselectively—with Co(II) complexes[45] and Pd(0) compounds,[46] leading to the corresponding hydroxyketones.

The reactions of dimethyl peroxide with metal cations described in this work exhibit some obvious similarities as compared to the condensed-phase chemistry. The FT-ICR experiments reveal the loss of methoxy radicals and the formation of $(CH_3O)M^+$. This process can be regarded as a formal oxidation of the metal (M(I) → M(II)), while the peroxide is reductively cleaved into an alkoxy radical and an alkoxide ligand which is complexed to the metal center. This process resembles the first step of the decomposition of diethyl peroxide in aqueous solution of $FeSO_4$ (Scheme 7). In the same context, the rearrangement of **2**/M^+ to **5**/M^+ (Scheme 2) may be considered as a unimolecular variant of the Fe(II)-catalyzed disproportionation of diethyl peroxide, which leads to the corresponding alcohol and ketone products. In spite of these formal analogies there are, of course, some differences due to possible interferences of the "solution environment". For example, the intramolecular redox reaction in the gas phase involves β-H transfer from the methoxy group to the metal, leading to the metal hydride species **3**/M^+. This process is unlikely to occur in aqueous solution, since immediate evolution of hydrogen gas by solvolysis of the metal hydride would be favored. However, with respect to solution chemistry, the current gas-phase data suggest an alternative mechanism to that shown in Scheme 7 in that formation of acetaldehyde can occur via abstraction of an α-hydrogen atom from the metal alkoxide by the ethoxide anion which is formed in the course of the electron transfer process. A distinction between both methods might be achieved by a kinetic study of metal-catalyzed peroxide decomposition at various pH values.

Conclusions

Gas-phase reactions of peroxides with bare and ligated third-row transition-metal cations represent simple model systems for the catalytic oxygenations and dioxygen activation processes which play an important role in chemistry. The results presented in this work reveal that oxygen transfer from dimethyl peroxide to the metal does not occur for the "late" transition metal cations Cr^+, Mn^+, Fe^+, and Co^+.

Not surprisingly, the initial step in the reaction of dimethyl peroxide with M^+ corresponds to the insertion of the metal into the weak O—O bond. This process turns out to be extremely exothermic with the consequence that the uni- and bimolecular chemistries are completely different, reflecting the energy content of the species. Although the mechanisms of the bond activation processes following the initial insertion step into the O—O bond are similar for the metal ions studied here, distinct metal-specific features evolve. In particular, for M = Mn, Fe, and Co an almost complete conversion of dimethyl peroxide into the methanol/formaldehyde complexes **5**/M^+ takes place, and this process resembles the Fe(II)-catalyzed decomposition of dialkyl peroxides in solution chemistry.

Finally, the comparison of gas- and condensed-phase metal-catalyzed decomposition of dialkyl peroxides reveals that electron transfer processes from the metal to the peroxo group are key steps in both media. However, there exist fundamental differences between the gas-phase chemistry and the reactions in the condensed phase. For example, in the gas phase the internal energy cannot be transferred to solvent molecules and the strictly uni- (ion beam) or bimolecular (FT-ICR) nature of the reactions renders the secondary reactions impossible, e.g., reactions of so-formed free alkoxy radicals. Nevertheless, the unique conditions prevailing in the gas phase permit the examination of the intrinsic properties of the species involved and trace them back to thermochemical and electronic differences as well as dynamic effects of the elementary steps.

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