# Gas-Phase Chemistry of Hydrogen Peroxide and Alkyl Hydroperoxides with “Bare” First-Row Transition-Metal Cations $Cr^+$−$Co^+$. Generation of $MO^+$ Cations Using $H_2O_2$ as Oxidant

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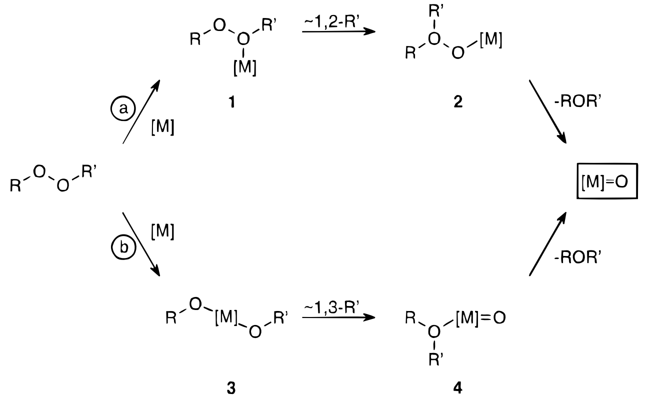
The unimolecular reactions of “bare” first-row transition-metal cations $Cr^+$−$Co^+$ complexed to small alkyl hydroperoxides and hydrogen peroxide have been examined by means of tandem mass spectrometry. In the metal-mediated reactions of the methyl, ethyl, and isopropyl hydroperoxides disproportionations of the peroxides dominate which involve insertion of the metal ion into the weak O−O bond followed by $\beta$-hydrogen shifts. These processes lead to competitive losses of water, aldehydes, or ketones as thermochemically favored neutral products. In addition, for $CH_3OOH/M^+$ unimolecular dehydrogenation to yield $M(OH_2)(CO)^+$ takes place. The metal complexes of *tert*-butyl hydroperoxide give rise to methanol as a side product *via* an analogous $\beta$-methyl migration and subsequent reductive elimination of methanol. However, for this complex the major reaction channel corresponds to water loss, which is rationalized by a multistep rearrangement. Interestingly, the observed reactivity patterns remain essentially unchanged irrespective of the nature of the metal. This may be attributed to the high thermodynamic stability of the products and the absence of other competing reaction channels. In contrast to the alkyl hydroperoxides, the hydrogen peroxide/$M^+$ complexes permit oxygen-atom transfer to the metal center to yield *inter alia* $MO(OH)^+$, $M(OH)^+$, and $MO^+$ cations. As shown previously, the latter can further be used as oxidants in the oxygenation of hydrocarbons.

## Introduction

Selective hydroxylation of C−H bonds in organic molecules represents one of the most important chemical transformations in small-scale laboratory, large-scale industrial, and biological processes.[1] In this respect, organic peroxides have attracted considerable attention as terminal oxidants, since they are not only easily available but also better fulfill safety requirements as compared to the use of (cheaper) dioxygen. However, the peroxidic oxygen needs to be activated by appropriate means, and often transition-metal compounds mediate this task. Although a variety of transition-metal catalysts for hydroxylation reactions are available, the knowledge about the detailed mechanism of peroxide activation at a molecular level is far from being complete.[1,2] Within this context, gas-phase experiments can complement classical mechanistic studies in the condensed phase, in that the intrinsic requirements for catalytic oxygen-atom transfer from a peroxide to an organic substrate can be evaluated without any complicating counterion, ligand, bulk, or solvent effects.[3]

### Scheme 1



From a chemical point of view, two conjectures for the activation of the peroxidic oxygen atoms by a transition-metal compound [M] are conceivable (Scheme 1):[4] (a) [M] may coordinate to the peroxo group as in **1**, which is followed by a 1,2-R′ transfer leading to the intermediate **2**. (b) Alternatively, [M] may oxidatively insert into the weak O−O bond of the peroxide to yield **3**, from which **4** may be formed via a 1,3-R′ migration. Both ways lead eventually to [M]═O species *via* reductive elimination of ROR′. Such transition-metal oxenoids have been proposed as active intermediates in numerous oxidations in the condensed as well as in the gas phase.[1,5]

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[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

[1] (a) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; Reidel: Boston, MA, 1984. (b) Ortiz de Montellano, P. R., Ed. *Cytochrome P-450: Structure, Mechanism and Biochemistry*; Plenum: New York, 1986. (c) Hill, C. L., Ed. *Activation and Functionalization of Alkanes*; Wiley: New York, 1989.

[2] Bruice, T. C. *Acc. Chem. Res.* **1991**, *24*, 243 and references cited therein.

[3] For recent reviews on the chemistry of transition-metal ions in the gas phase, see: (a) Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121. (b) Eller, K. *Coord. Chem. Rev.* **1993**, *126*, 93. (c) Freiser, B. S. *Acc. Chem. Res.* **1994**, *27*, 353.

[4] Bach, R. D.; Su, M.-D.; Schlegel, H. B. *J. Am. Chem. Soc.* **1994**, *116*, 5379.

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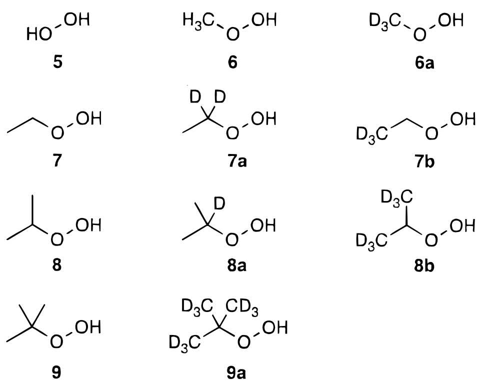
**Chart 1**



Recently,[6] it has been demonstrated that late transition-metal oxides such as CoO$^+$ oxidize alkanes to the corresponding alcohols and even benzene[7] to phenol (eq 1). Therefore, the question arises if it is possible to

$$\mathrm{CoO^+ + R{-}H \rightarrow Co^+ + R{-}OH} \qquad (1)$$

generate, for example, CoO$^+$ by the reaction of “bare” Co$^+$ cations with organic peroxides, thus opening a route for the catalytic oxidation of hydrocarbons in the gas phase[5] by using peroxo compounds as terminal oxygen donors.

For dialkyl peroxides O−O bond activation of the peroxides by “bare” and ligated transition-metal cations in the gas phase does indeed occur (Scheme 1, pathway b).[8] However, no evidence for O-atom transfer from these peroxides to metal cations has been observed experimentally, except for the highly oxophilic early transition-metal cations, for which O-atom capture from almost any oxygen containing compound is more or less inevitable.[8b] Instead, for most of the d-block metal cations intramolecular redox processes take place which lead to a formal disproportionation of the peroxides to the corresponding alcohols and carbonyl compounds. Obviously, for the activation of the peroxidic oxygen according to the mechanisms proposed in Scheme 1, the nature of the migrating group R′ has to be altered in order to facilitate its transfer. One should expect that for R′ = H the 1,2- or 1,3-migration (Scheme 1) can more easily be realized. In this article, we report the results of a mass-spectrometric study of the unimolecular fragmentations of hydroperoxides (Chart 1) complexed to “bare” M$^+$ cations (R′ = H; M = Cr, Mn, Fe, Co), and we will present evidence for the formation of MO$^+$ cations from “bare” M$^+$ using hydrogen peroxide as an O-atom transfer reagent.

## Experimental Section

The experiments were performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sectors), which has been described elsewhere.[9] Hydroperoxide/M$^+$ complexes were generated by chemical ionization of ca. 5:1 mixtures of the peroxide and $Cr(CO)_6$, $Mn_2(CO)_{10}$, $Fe(CO)_5$, and $Co(CO)_3(NO)$, respectively.[8a] The ions of interest, having 8 keV kinetic energy, were mass-selected by using B(1)/E(1) at a resolution of $m/\Delta m \approx 3000$. Unimolecular dissociations of metastable ions (MI mass spectra) in the field-free region preceding the second magnet were recorded by scanning B(2), and for obtaining collisional activation (CA) mass spectra, helium (80% transmission (T)) was admitted to a collision cell that is located between E(1) and B(2). The error of the MI and CA mass spectra is estimated not to exceed ±10%. MS/MS/MS experiments[10] were performed by selecting the fragment ions of interest by means of B(2), and the collision-induced fragmentations (He, 80% T) occurring in the subsequent field-free region were monitored by scanning E(2); these experiments will be referred to as MI/CA spectra. The sensitivity in MS/MS/MS experiments is less as compared to that of the MS/MS studies, and thus the error is larger (±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.

$H_2O_2$ (35% in $H_2O$) and *tert*-butyl hydroperoxide (70% in $H_2O$) were commercially available and used after purification (extraction with diethyl ether and removal of the solvent). Methyl hydroperoxides **6** and **6a** were synthesized by alkylation of $H_2O_2$ with dimethyl sulfate ([$D_6$] dimethyl sulfate) under basic conditions.[11] Ethyl (**7**−**7b**) and isopropyl hydroperoxides (**8**−**8b**) were prepared by reacting the corresponding (labeled) chloride Grignard reagents with oxygen,[12] and [$D_9$]-*tert*-butyl hydroperoxide (**9a**) was synthesized from [$D_9$]-*tert*-butyl chloride and $H_2O_2$ using silver trifluoroacetate as coupling reagent.[13] All products were purified by distillation and characterized by $^1$H-NMR spectroscopy.[14] The labeled compounds generally contained >98 atom % D.

Due to decomposition, alkyl hydroperoxides and $H_2O_2$ cannot be introduced into the mass spectrometer using the commercial stainless steel/glass inlet system; instead, a home-built[8a] glass/Teflon inlet system was used in which decomposition of the proxides can mostly be avoided. For $H_2O_2$ however, to some extent decomposition in the ion source was observed giving rise to molecular oxygen as one of the main products. Nevertheless, the signal for the $H_2O_2^{+\bullet}$ radical cation is by far more intense than that of isobaric $^{16}O^{18}O^{+\bullet}$, which can be deduced from the intensity of the $^{16}O_2^{+\bullet}$ ion by considering the natural abundance of $^{18}O$. This indicates that isobaric impurities of $M(^{16}O^{18}O)^+$ complexes are negligible. *Note that the handling of hydroperoxides as well as concentrated $H_2O_2$ demands appropriate safety precautions.*

## Results and Discussion

Table 1 shows the neutral products of the unimolecular dissociations of alkyl hydroperoxide/M$^+$ complexes (M = Cr−Co). In general, the observed reactions are qualitatively and in most cases even quantitatively the same for each hydroperoxide and do not depend much on the nature of the metal. This result may be due to

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(11) Rieche, A.; Hitz, F. *Chem. Ber.* **1929**, *62*, 2458.

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(14) (a) Ward, G. A.; Mair, R. D. *Anal. Chem.* **1969**, *41*, 538. (b) Kropf, H.; Bernert, C.-R. *Z. Anal. Chem.* **1969**, *248*, 35. (c) Skowronska-Ptarinska, M.; Pasynkiewicz, S.; Sieczek, E. *J. Organomet. Chem.* **1981**, *206*, 1.

**Table 1. Intensities for Mass Differences (in amu) Observed in the Unimolecular Fragmentations of Metastable Alkyl Hydroperoxide/M$^+$ Complexes[a]**

| | $\Delta m$ | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $-2$ | $-15$ | $-18$ | $-28$ | $-30$ | $-31$ | $-32$ | $-44$ | $-45$ | $-46$ | $-58$ | M$^+$ |
| **6**/Cr$^+$ | 18 | | 55 | | 14 | 4 | 3 | | | | | 6 |
| **6**/Mn$^+$ | 5 | | 79 | | 10 | 2 | 2 | | | | | 2 |
| **6**/Fe$^+$ | 81 | | 13 | | 3 | 1 | 1 | | | | | 1 |
| **6**/Co$^+$ | 33 | | 42 | | 16 | 3 | 1 | | | | | 5 |
| **7**/Cr$^+$ | | | 90 | 1 | | | | 3 | 2 | 1 | | 3 |
| **7**/Mn$^+$ | | | 96 | | | | | 2 | 1 | | | 1 |
| **7**/Fe$^+$ | | | 94 | 3 | | | | 1 | 1 | | | 1 |
| **7**/Co$^+$ | | | 97 | 1 | | | | 1 | | | | 1 |
| **8**/Cr$^+$ | | | 97 | | | | | | | | 1 | 2 |
| **8**/Mn$^+$ | | | 98 | | | | | | | | 1 | 1 |
| **8**/Fe$^+$ | | | 98 | | | | | | | | 1 | 1 |
| **8**/Co$^+$ | | | 98 | | | | | | | | 1 | 1 |
| **9**/Cr$^+$ | | 2 | 69 | | | | 29 | | | | | |
| **9**/Mn$^+$ | | 1 | 98 | | | | 1 | | | | | |
| **9**/Fe$^+$ | | 9 | 88 | | | | 3 | | | | | |
| **9**/Co$^+$ | | | 98 | | | | 2 | | | | | |

[a] Intensities are normalized to $\sum = 100\%$. Intensities less than 1% are omitted.

the high thermodynamic stability of the products formed in the reactions, i.e. water and aldehydes/ketones, and to the absence of other pathways which energetically are able to compete effectively. The reactivity of $CH_3OOH/M^+$ complexes constitutes an exception, since the relative abundance of dehydrogenation is much more intense for M = Fe as compared to M = Cr, Mn, and Co. This can be explained by a competition of the fragmentation channels, which lead to dehydrogenation and water losses (see below). In the following, we will discuss the fragmentations of the Co$^+$ complexes in detail as representatives for all other metals investigated. The data derived from the MI mass spectra of the labeled and unlabeled alkyl hydroperoxide/Co$^+$ complexes are given in Table 2.

**Unimolecular Decomposition Reactions of 6/Co$^+$, 7/Co$^+$, and 8/Co$^+$.** For the lowest homologue, $CH_3OOH/Co^+$ (**6**/Co$^+$), the dominant reactions correspond to losses of neutral dihydrogen ($\Delta m = 2$), water ($\Delta m = 18$), and formaldehyde ($\Delta m = 30$), respectively. These products can be accounted for by involving an initial insertion of the Co$^+$ cation into the peroxidic O$-$O bond (Scheme 2), followed by transfer of a $\beta$-hydrogen atom from the methoxy group[8c,15] to the hydroxy functionality to yield the bis-ligated complex **10**. The overall process is very exothermic,[16,17] and internally excited **10** can subsequently decompose either by loss of the water and/or the formaldehyde ligands or by dehydrogenation of the formaldehyde molecule within the complex[8a] to yield **14** (Scheme 3). The structure of **14** has been probed by collisional activation of the daughter ion formed by dehydrogenation, and the MI/CA mass spectrum shows three intense processes corresponding to the losses of water, carbon monoxide, and the regeneration of the metal cation. The mechanistic scenario presented here is completely in line with the mass spectrum of **6a**/Co$^+$ in which losses of $D_2$ ($\Delta m = 4$), HDO ($\Delta m = 19$), and $CD_2O$ ($\Delta m = 32$) are observed. Overall, the reaction of **6**/Co$^+$ can be classified as an intramolecular redox process in which the hydroperoxide disproportionates to water and formaldehyde. Thus, instead of the desired transfer for the hydroperoxo proton in the sense of Scheme 1, $\beta$-hydrogen transfer from the methoxy group (either direct or via the metal center) to the hydroxy moiety predominates. The elimination of neutral methanol ($\Delta m = 32$), which would be indicative for the formation of the reactive CoO$^+$ cation, is more or less negligible.

Similar mechanisms account for the unimolecular reactions of the Co$^+$ complexes of ethyl and isopropyl hydroperoxide, **7** and **8**. Here, the situation is even more simple, since in the corresponding intermediates **11** and **12** (Scheme 2) water represents the most weakly bound ligand[18,19] and formation of **14** *via* loss of methane from **11** or ethane from **12** would involve C$-$C bond activation which is expected to be less facile. As a consequence, unimolecular loss of water ($\Delta m = 18$) by and large dominates in the mass spectra of **7**/Co$^+$ and **8**/Co$^+$, while losses of the corresponding carbonyl compounds (acetaldehyde, $\Delta m = 44$, and acetone, $\Delta m = 58$) hardly compete. Again, the isotope distributions for the deuterated peroxides are in line with the mechanism proposed in Scheme 2. The minor amounts of H/D exchange processes in the water loss channel ($H_2O$, $\Delta m = 18$; $D_2O$, $\Delta m = 20$) are not at all unexpected[20] and do not conflict with the proposed mechanism. Furthermore, since no significant changes in the product branching ratios are observed for the deuterated peroxides, unusually large kinetic isotope effects or processes such as hydrogen-atom tunneling are not likely to be involved in the formation and decomposition of **11** and **12**.

A minor product channel (1%) leads to the elimination of neutral ethylene from **7**/Co$^+$. The product corresponds most likely to $Co(OH)_2^+$ ions, since, assuming a simple additivity scheme,[21,22] thermodynamic data indicate that $Co(OH)_2^+$ is ca. 12 kcal/mol more stable than $(H_2O)CoO^+$; however, additivity does not always hold true.[23] Nevertheless, both these ions can be regarded as equivalents and precursors for CoO$^+$, since the metal is in the same formal oxidation state, cobalt(III), and water loss from either isomer would lead to the metal

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(15) For previous examples of $\beta$-H and $\beta$-CH$_3$ transfers in cationic metal alkoxides, see: (a) Cassady, C. J.; Freiser, B. S.; McElvany, S. W.; Allison, J. *J. Am. Chem. Soc.* **1984**, *106*, 6125. (b) Schröder, D.; Schwarz, H. *Angew. Chem.* **1990**, *102*, 925; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 910. (c) Fiedler, A.; Schröder, D.; Schwarz, H.; Tjelta, B. L.; Armentrout, P. B., submitted for publication.

(16) The reaction exothermicity ($\Delta H_R$) for $Co^+ + CH_3O{-}OH \rightarrow (CH_2O)Co(OH_2)^+$ exceeds 130 kcal/mol.

(17) Thermochemical data were taken from: (a) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. (b) Lias, S. G.; Liebman, J. F.; Levin, R. D.; Kafafi, S. A. *NIST Standard Reference Database, Positive Ion Energetics*, Version 2.01; NBS: Gaithersburg, MD, Jan 1994. (c) Martinho-Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629. For recent surveys of accurate thermodynamics of small organometallic ions, see: (d) Armentrout, P. B.; Kickel, B. L. In *Organometallic Ion Chemistry*; Freiser, B. S., Ed.; Kluwer: Dordrecht, The Netherlands, 1995; p 1. (e) Freiser, B. S. *Ibid.*

(18) Presently, no data are available for the binding energy of carbonyl compounds to Co$^+$. However, for the group 8 metal Fe$^+$ carbonyl compounds are more strongly bound to the metal than water, and it is reasonable to extrapolate this trend to Co$^+$; see also refs 17 and 19.

(19) Schröder, D.; Schwarz, H. *J. Organomet. Chem.*, in press.

(20) (a) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1976**, *98*, 7445. (b) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998. (c) Prüsse, T.; Schwarz, H. *Organometallics* **1989**, *8*, 2856.

(21) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

(22) For an application to an organometallic system, see: Becker, H.; Schröder, D.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.* **1994**, *116*, 1096.

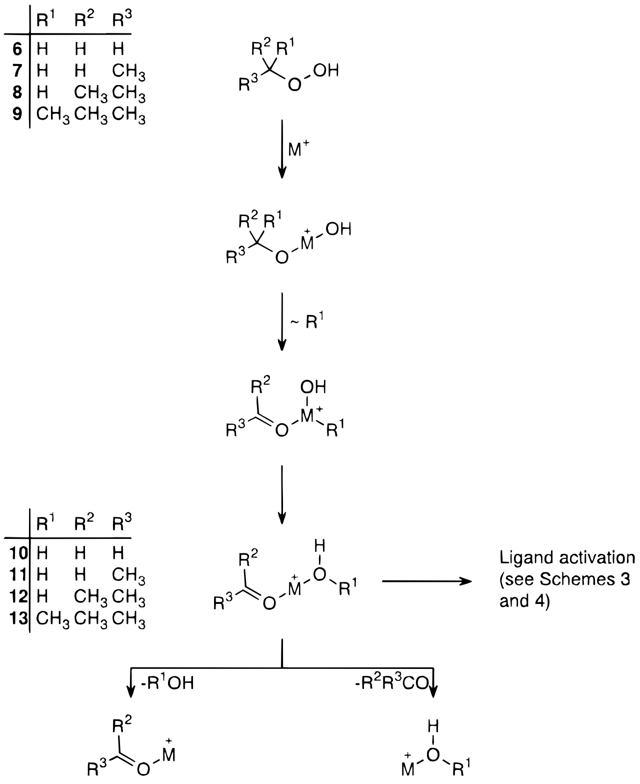
(23) Examples: (a) Reference 17b. (b) Rosi, M.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1990**, *92*, 1876. (c) Tjelta, B. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 5531.

**Table 2. Intensities for Mass Differences (in amu) Observed in the Unimolecular Fragmentations of Metastable 6/Co$^+$−9/Co$^+$ and Their Isotopologues**[a]

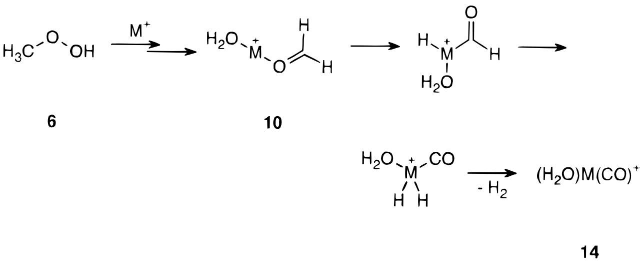
| | Δ*m* | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | −2 | −4 | −18 | −19 | −20 | −28 | −30 | −31 | −32 | −34 | −35 | −44 | −45 | −47 | −58 | −64 | M$^+$ |
| **6**/Co$^+$ | 33 | | 42 | | | | 16 | 3 | 1 | | | | | | | | 5 |
| **6a**/Co$^+$ | | 24 | | 57 | | | | | 15 | 1 | 1 | | | | | | 2 |
| **7**/Co$^+$ | | | 97 | | | 1 | | | | | | 1 | | | | | 1 |
| **7a**/Co$^+$ | | | 2 | 93 | 1 | | 1 | | | | | | 2 | | | | 1 |
| **7b**/Co$^+$ | | | 93 | 3 | 1 | | 1 | | | | | | | 1 | | | 1 |
| **8**/Co$^+$ | | | 98 | | | | | | | | | | | | 1 | | 1 |
| **8a**/Co$^+$ | | | 2 | 95 | | | | | | | | | | | 2 | | 1 |
| **8b**/Co$^+$ | | | 94 | 3 | 1 | | | | | | | | | | | 1 | 1 |
| **9**/Co$^+$ | | | 98 | | | | | | 2 | | | | | | | | |
| **9a**/Co$^+$ | | | | 97 | | | | | | | 3 | | | | | | |

[a] Intensities are normalized to $\Sigma = 100\%$. Intensities less than 1% are omitted.

**Scheme 2**



**Scheme 3**



oxenoid. Unfortunately, the intensity of the Co(OH)$_2$$^+$ signal in the MI spectra of **7**/Co$^+$ is almost negligible.

In conclusion, the hydroperoxide complexes **6**/M$^+$−**8**/M$^+$ only reveal minor amounts of oxygen atom transfer products, although one expects that for hydroperoxides a migration of R′ = H according to Scheme 1 should be facilitated as compared to the reactions of dialkyl peroxide/M$^+$ complexes (R′ = alkyl).[8c] Instead, β-hydrogen shifts from the alkoxy group in **3** to the metal center dominate the gas-phase reactions of **6**/M$^+$−**8**/M$^+$, leading to water, aldehydes, and ketones as neutral products. Two strategies can now be pursued in order to change the reactivity toward the desired oxygen transfer: (i) If the α-position of the hydroperoxide alkyl group is suitably substituted with groups rendering the β-shifts more difficult, the desired oxygen transfer possibly may occur. From our studies of dialkyl peroxide/Fe$^+$ complexes[8c] it is known that a β-methyl shift is hindered by a barrier higher as compared to a β-hydrogen shift. Thus, for the *tert*-butyl hydroperoxide/M$^+$ complexes, which are completely methylated at the peroxy carbon, the mechanism commencing with a β-methyl shift as depicted in Scheme 2 (**9**/M$^+$ → **13**) should be disfavored. Therefore, **9**/M$^+$ is expected to be a promising candidate for an oxygen atom transfer. (ii) All reactions involving the α-position of the peroxides are rendered impossible for the M$^+$ complexes of hydrogen peroxide. Thus, the parent compound, $H_2O_2$, is expected to yield metal oxenoid ions *via* oxygen transfer and losses of water. In the following sections we will discuss the gas-phase chemistry of these two compounds, again exemplarily for the Co$^+$ complexes.

**Gas-Phase Reactivity of 9/Co$^+$.** In the MI mass spectra of *tert*-butyl hydroperoxide/Co$^+$, **9**/Co$^+$, two fragmentations[24] are observed which can be attributed to the loss of water (Δ*m* = 18) as the by far predominating reaction channel and the expulsion of methanol (Δ*m* = 32) as a side reaction. The data of the [D$_9$]-labeled isotopologue **9a**/Co$^+$ agree with this assignment: Exclusive generation of neutral HDO (Δ*m* = 19) indicates that the intact hydroxyl group is involved,[25] and the signal for methanol losses is shifted to Δ*m* = 35, which points to the participation of an intact $CD_3$ group. In mechanistic terms, the methanol loss can easily be rationalized by the mechanism depicted in Scheme 2 involving a β-methyl transfer to the metal center, subsequent formation of bis-ligated intermediate **13**, and, eventually, expulsion of the more weakly bound methanol ligand. Obviously, the β-shift is indeed disfavored by a complete methyl substitution at the peroxy carbon of the hydroperoxide. However, instead of oxygen transfer and formation of CoO$^+$ according to Scheme 1 a new process is observed, which gives rise to water as neutral product. Unfortunately, due to the low absolute intensity of the **9**/Co$^+$ ions, which had to be highly resolved to exclude isobaric impurities related to the proton bound dimer of acetone and *tert*-butyl

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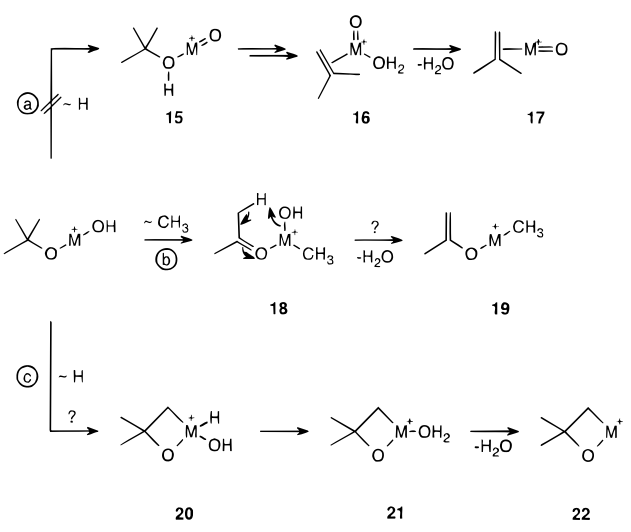
[24] In addition, the Cr$^+$−Fe$^+$ complexes of **9** exhibit very minor amounts of methyl losses, which are shifted to Δ*m* = 18 for **9a**/M$^+$ ($CD_3^\bullet$ losses).

[25] For M = Cr−Fe partial H/D exchange is observed as indicated by the formation of HDO and $D_2O$ from **9a**/M$^+$ in a ca. 5:1 ratio.

**Scheme 4**



hydroperoxide, we could not characterize the daughter ions by the corresponding MI/CA spectrum. Thus, we cannot satisfactorily answer the questions by which pathways water is eliminated from **9**/$Co^+$. Therefore, in the next section we will discuss three chemically reasonable proposals, which are depicted in Scheme 4.

At first, we assume that a hydrogen shift from the OH group to the oxygen atom of the *tert*-butoxy ligand occurs according to Scheme 1 (pathway a in Scheme 4) to form intermediate **15**, which may eliminate water *via* **16** to give rise to the ionic product **17**. While water elimination from alcohols is known for “bare” metal cations[26] as well as metal oxide cations,[27] for the latter species intense concomitant losses of neutral alkenes and formation of the corresponding $M(OH)_2^+$ ions are observed. Neither the MI nor the CA mass spectra of **9**/$Co^+$ exhibit elimination of isobutene concomitant with the formation of $Co(OH)_2^+$, and in the CA spectrum the $CoO^+$ signal does not exceed 1%, though the generation of $CoO^+$ from **17** should be facile. Thus, we cannot present any experimental support for the occurence of this pathway and, hence, conclude that oxygen transfer from the hydroperoxide to the metal does not take place.

As a second possibility, we consider pathway b in Scheme 4, which involves a $\beta$-methyl shift to the metal center leading to **18**; this species is also postulated as an intermediate *en route* to the methanol loss from **9**/$Co^+$. Water can be formed from **18** *via* a six-membered transition structure leading to the enolate complex **19**. It is quite clear that this mechanistic picture does not play a role for the water losses from **7**/$Co^+$ and **8**/$Co^+$, since then $H_2O$ should be formed from **7a**/$Co^+$ and **8a**/$Co^+$ and, correspondingly, HDO from **7b**/$Co^+$ and **8b**/$Co^+$. However, if the ionic product of the water losses was **19**, one would expect signals for $Co(CH_3)^+$ and $Co(OC_3H_5)^+$ in the CA mass spectrum of **9**/$Fe^+$; these signals are absent. Therefore, although we cannot fully exclude mechanism b, which is tempting due to the six-membered transition structure for the reaction step **18** → **19**, we assume that it does not account for the majority of the water loss from **9**/$Co^+$.

**Table 3. Intensities for Collisional Activation Fragmentation Processes Observed for the $H_2O_2$/$M^+$ Complexes**[a]

| | Δ*m* | | | | |
|---|---|---|---|---|---|
| | −1 | −16 | −17 | −18 | $M^+$ |
| **5**/$Cr^+$ [b] | 3 | 3 | 17 | 66 | 11 |
| **5**/$Mn^+$ | 4 | 1 | 50 | 36 | 9 |
| **5**/$Fe^+$ [b] | 6 | 3 | 43 | 37 | 11 |
| **5**/$Co^+$ | 4 | 2 | 20 | 68 | 6 |

[a] Intensities are normalized to $\sum = 100\%$. [b] Intensities were corrected for contributions of isobaric $^{50}Cr(H_2O)_2^+$ and $^{54}Fe(H_2O)_2^+$ ions.

Finally, pathway c describes a 1,3-elimination of water giving rise to the metallaoxetane **21** as intermediate, which upon water loss leads to **22** as ionic product. The formation of metallacyclobutanes[28] as well as metallaoxetanes[29] have been studied previously, and the decomposition reactions are quite well-known. According to Scheme 4, 1,3-elimination **9**/$M^+$ → **21** must proceed *via* intermediate **20**, which bears a metal center in the formal oxidation state +5, which seems to be quite unplausible. However, rearrangement of the O−O inserted species to **21** may also occur directly *via* a multicentered transition structure.[30] Therefore, on the basis of our data, we unfortunately cannot decide whether pathway c is operative or not, and for the time being we can only state that the experimental findings are not in conflict with it.

In summary, oxygen transfer to generate cationic metal oxenoids from “bare” metal ions in the gas phase turned out to be unachievable using dialkyl peroxides and alkyl hydroperoxides as oxidants. Therefore, we studied the gas-phase reactions of the parent compound, i.e. hydrogen peroxide, with the “bare” metal cations $Cr^+$−$Co^+$.

**Generation of $MO^+$ Cations from $H_2O_2$/$M^+$ Complexes.** The $H_2O_2$/$M^+$ ions generated by chemical ionization of a mixture of $H_2O_2$ and the corresponding metal carbonyl compound do not undergo any significant unimolecular processes. This is not unexpected, if one considers the few degrees of freedom in $[M,H_2,O_2]^+$ which are available for the storage of internal energy to yield metastable ions undergoing delayed dissociation in the microsecond time window. However, upon collisional activation (Table 3) the following reaction channels are observed, again qualitatively independent on the nature of the metal: Generation of $[M,O_2,H]^+$ ($\Delta m = 1$) resulting from the loss of a hydrogen atom and most likely corresponding to an $O{=}M{-}OH^+$ structure,[31] $M(H_2O)^+$ ($\Delta m = 16$, loss of an oxygen atom), $M(OH)^+$ ($\Delta m = 17$, expulsion of a hydroxyl radical), the formation of $MO^+$ ($\Delta m = 18$, loss of water), and the loss

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of the complete ligand to yield $M^+$. The base peak in the CA spectra of **5**/$Cr^+$ and **5**/$Co^+$ corresponds to the production of $MO^+$, and this observation demonstrates that—upon collisional activation—hydrogen peroxide is capable to transfer an oxygen atom to late transition-metal cations (eq 2), a process which is exothermic by

$$M^+ + H_2O_2 \rightarrow MO^+ + H_2O \tag{2}$$

ca. 41 kcal/mol for the $Co^+$ complexes and would even be exothermic for **5**/$M^+$, if we assume that BDE($M^+$−$OH_2$) ≈ BDE($M^+$−$O_2H_2$).[17c] This assumption is supported by the similar proton affinities of $H_2O$ and $H_2O_2$, since *cum grano salis*, the proton affinities of closed-shell ligands L parallel the bond dissociation energies of the corresponding $M^+$−L complexes.[17a]

In the CA spectra of **5**/$Mn^+$ and **5**/$Fe^+$, losses of hydroxyl radicals correspond to the base peak, but the formation of $MO^+$ cations is also a major process. From earlier studies[8] it is known that the electronic ground states of $Mn^+$ ($4s^13d^5$) and $Fe^+$ ($4s^13d^6$) favor the formation of only one covalent metal−ligand bond.[32] Thus, the loss of an $OH^\bullet$ radical leads to the generation of the preferred ligand sphere for these systems, i.e. the $M(OH)^+$ cations, which parallels Fenton's chemistry in the condensed phase.[33]

## Conclusions

A huge body of experimental as well as theoretical investigations has been reported in the last few years dealing with the formation, reactivity, and thermochemical features of metal−oxide cations in the gas phase.[5] However, the oxidizing potential of peroxides so far has been unexplored as far as the gas phase is concerned, though in condensed phase chemistry peroxides play an important role for the formation of [M]═O systems and oxygen transfer reactions.[1] The present study is the first example succeeding in the activation of a peroxidic oxygen atom by "bare" late transition-metal cations.

In previous studies[8] it has been demonstrated for dialkyl peroxide/$M^+$ complexes that reactions involving the α-position of peroxides lead to reaction pathways which are energetically located below the oxygen-activation channel. The latter is observed only for the early transition-metal cations which exhibit extraordinary high oxophilicities. Similar processes render oxygen transfer to late transition metals unachievable for alkyl hydroperoxides. Therefore, only the parent compound $H_2O_2$, which does not bear any substituents in the α-position, produces $MO^+$ ions, if reacted with "bare" metal cations.

Obviously, for the realization of selective O-atom transfer from an alkyl hydroperoxide to a metal, the reactivity of "bare" metal cations (as well as the "bare" $MO^+$ products) is simply too high. Possibly, a suitably ligated peroxide/$M^+$ complex is able to direct the reactivity of the system toward oxygen transfer. Some examples for distinct and unexpected reactivity shifts in gas-phase reactions have recently reported which are due to pronounced ligand effects.[34] A detailed investigation addressing this question is in progress.

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