Bimolecular Gas-Phase Reactions of d-Block Transition-Metal Cations with Dimethyl Peroxide: Trends Across the Periodic Table

Ralf Wesendrup, Christoph A. Schalley, Detlef Schröder and Helmut Schwarz*

Abstract: The bimolecular gas-phase reactions of d-block transition-metal cations M^+ with dimethyl peroxide were screened by means of Fourier transform ion cyclotron resonance mass spectrometry. The rich chemistry can be classified into four types of reactions: i) Oxygen-atom transfer to generate MO^+, ii) elimination of radicals, mostly $CH_3O^{\bullet}$, iii) intramolecular redox reaction of dimethyl peroxide to form CH_3OH, CH_2O and CO, and iv) charge transfer from the metal cation to produce $CH_3OOCH_3^+$. Some general trends became apparent from this study. For example, the "early" transition metals almost exclusively induce oxygen transfer to generate MO^+, in line with the notoriously high oxophilicities of these metals, and electron transfer is only observed for Zn^+ and Hg^+. Both the radical loss and the disproportionation reaction emerge from a rovibrationally highly excited insertion intermediate $(CH_3O)_2M^+$, and for the first-row metals the branching ratio of the competing processes seems to be affected by the M^+-OR bond strengths as well as the electronic ground-state configurations of M^+. For the 4d and 5d cations Ru^+-Ag^+ and Pt^+-Au^+, respectively, products resulting from intramolecular redox reactions dominate; this probably reflects the higher propensity of these metal ions to facilitate β-hydrogen atom shifts.

Keywords
gas-phase chemistry · mass spectrometry · periodic trends · peroxides · transition-metal ions

Introduction

Oxidation reactions are among the most important chemical processes in areas encompassing chemical synthesis, large-scale industrial applications and biological systems.[1] In particular, the hydroxylation of hydrocarbons, that is the transformation $R-H \rightarrow R-OH$ by O-atom transfer is of enormous economic importance and scientific interest.[2] In comparison to other common oxidants, peroxo compounds ROOR have proven to be especially valuable reagents in that their reactivity can be tuned by choice of appropriate substituents or the metal catalysts employed. Thus, peroxides are widely used as radical sources in technical processes such as radical polymerization, or as efficient oxygen-atom donors in oxidation reactions; in the latter transition-metal complexes quite often serve as catalysts.[3a, b] Moreover, peroxides play a key role as intermediates in biological systems,[3c, d] for example in prostaglandin biosynthesis,[3e] and also in atmospheric chemistry.[3f] The obvious importance of peroxo compounds contrasts sharply with the rather limited knowledge of mechanistic details of peroxide activation by transition metals. Gas-phase studies are a valuable way to investigate elementary steps of organometallic reactions, because they provide fundamental information on the intrinsic properties and reactivities of metal ions in the absence of complicating bulk effects such as solvent, counterion, or aggregation phenomena.[4] Surprisingly enough, the gas-phase chemistry of metal cations with peroxides has been almost completely neglected so far.[5] Recently, we initiated a systematic mass spectrometric study of the metal-induced chemistry of peroxo compounds[6] aimed at elucidating the mechanistic details of metal-mediated peroxide activation and oxygen-transfer processes. In this paper we will present the results of the bimolecular reactions of "naked" transition-metal cations with the most simple dialkyl peroxide, dimethyl peroxide, under the conditions of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. This is the first exhaustive study including nearly all 3d, 4d and 5d transition-metal ions; technetium was not included for obvious reasons, while for osmium the ion yields were too low for a detailed investigation. In addition, we have examined the reactions of the first-row transition metals with [1,1,1-D_3] and [D_6] dimethyl peroxide.

Experimental Section

The experiments were performed with a Spectrospin CMS 47X FT-ICR mass spectrometer equipped with an external ion source and a superconducting magnet (Oxford Instruments, 7.05 Tesla); the instrument and its operation have been described in detail previously [7]. In brief, M^+ ions were generated by laser desorption/laser ionization by focussing the beam of a Nd/YAG laser (1064 nm) onto a pure metal target [8]. For the generation of Hg^+ an alloy of tin, silver and mercury was used instead of the pure metal. The cations were extracted from the ion source and transferred to the analyzer cell by a system of electric potentials and lenses. The isolation of the most abundant metal isotope and all subsequent isolation steps were performed by FERETS [9], a computer-controlled ion-ejection protocol which combines single-frequency ion-ejection pulses with frequency sweeps to optimize ion isolation. Subsequently, the ions were thermalized by collisions with pulsed-in

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[*] H. Schwarz, R. Wesendrup, C. A. Schalley, D. Schröder
Institut für Organische Chemie der Technischen Universität Berlin
Straße des 17. Juni 135, D-10623 Berlin (Germany)
Telefax: Int. code + (30)314-21102
e-mail: schw0531@zrzsp5.chem.tu-berlin.de

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argon gas, and the thermalized ions were carefully reisolated to avoid off-resonance excitation [10]. Thermalization was assumed to be complete when no further change in reactivity occurred upon increasing the number of collisions with argon [11]. Dimethyl peroxide was admitted to the FT-ICR cell through a leak valve at a pressure of about 10^{-8} mbar. All functions of the instrument were controlled by a Bruker Aspect 3000 minicomputer.

The different isotopologues of dimethyl peroxide were synthesized by alkylation of dihydrogen peroxide with dimethyl sulfate under basic conditions and purified by distillation [12]. Since an inexpensive synthesis of pure $[1,1,1\text{-}D_3]$ dimethyl peroxide is not straightforward, a 1:1 mixture of $[D_6]$ dimethyl sulfate and $[D_0]$ dimethyl sulfate was used in the above reaction, resulting approximately in a 1:2:1 ratio of $[D_0]$, $[D_3]$ and $[D_6]$ dimethyl peroxide. The ionic products formed in the ion/molecule reactions with M^+ can be traced back to the "pure" $[D_0]$, $[D_3]$ and $[D_6]$ precursors, at least qualitatively, so the availability of a particular isotopologue is not required. Prior to the introduction into the ICR mass spectrometer, dimethyl peroxide was subjected to three freeze–thaw–pump cycles to remove noncondensable gases.

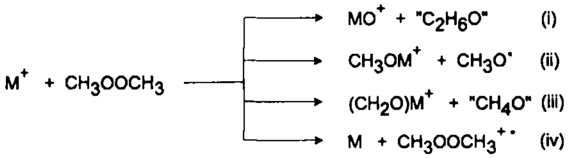
Table 1. Product distribution for the reactions of "naked" M^+ with dimethyl peroxide [a].

	Sc^+	Ti^+	V^+	Cr^+	Mn^+	Fe^+	Co^+	Ni^+	Cu^+	Zn^+
MO^+	100	100	40							
$MOH^{\bullet}$										
$(CH_2O)_2M^+$				34		7	25	50	25	
CH_3OM^+			60	66	100	93	75	50		70
$(CH_2O)M^+$									50	
$(CH_2O)MOCH_3^+$									25	
$C_2H_6O_2^+$										30
	Y^+	Zr^+	Nb^+	Mo^+	(Tc^+)[b]	Ru^+	Rh^+	Pd^+	Ag^+	Cd^+
MO^+	100	100	73							
MOH^+			14	13						
MCO^+			3			44	47	19		
$(CO)MH^+$			5	29		23	13	22		
$(CH_2O)M^+$			5	9		33	29	59	100	
CH_3OM^+				49			4			
$(CH_2O)MCO^+$							7			
$(CH_2O)MOCH_3^+$										100
	La^+	Hf^+	Ta^+	W^+	Re^+	Os^+[b]	Ir^+	Pt^+	Au^+	Hg^+
MH^+					100		33			
MH_2^+								43	49	
MO^+	100	100	100	80						
MOH^+				6						
MCO^+				5			40	57	21	
$(CO)MH^+$				4			27			
$(CH_2O)M^+$				5					30	
$C_2H_6O_2^+$										100

[a] Intensities are normalized to $\sum$products = 100%. [b] These metal ions have not been studied for reasons given in the Experimental Section.

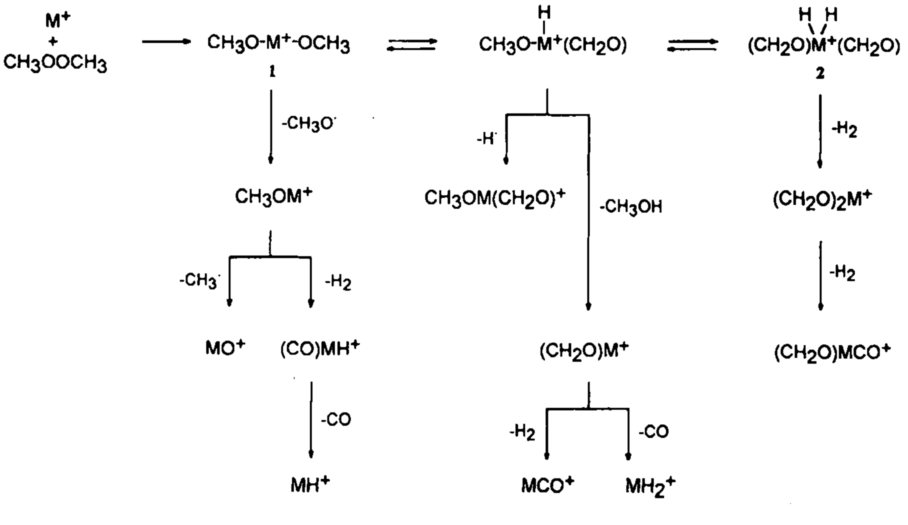
Results and Discussion

A characteristic feature of peroxides is their very weak O–O bond (e.g., BDE = 37 kcal mol^{-1} for dimethyl peroxide).[13] Accordingly, this linkage is initially attacked by the metal cation to yield the inserted bismethoxide $CH_3O{-}M^+{-}OCH_3$ (**1**).[14] While the exact energetics of the complexes thus formed are not known, this insertion is, of course, very exothermic for all metal ions. Therefore, once **1** is formed in an ion/molecule reaction of dimethyl peroxide with M^+, it will be rovibrationally highly excited and it will give rise to a variety of products. These products can be classified in terms of four different types of reaction (Scheme 1): i) Oxygen-atom transfer from the peroxide to the metal, leading to the formation of a metal oxocation MO^+; ii) elimination of open-shell neutrals, most often a methoxy radical; iii) intramolecular redox reactions resulting in the formation of methanol, formaldehyde, carbon monoxide or dihydrogen as neutrals; and iv) electron transfer to form the neutral metal atom and the molecular cation of dimethyl peroxide. Although it is self-evident that the mechanistic details for generating the various products are likely to be metal-dependent, we will use the classification depicted in Scheme 1 to assess periodic trends within the d-block transition metals.[15]



Scheme 1.

Table 1 sums up the relative intensities of the ionic products resulting from the reactions of M^+ and dimethyl peroxide. Structures are inferred based on plausible reaction processes, isotopic labelling and ligand exchange experiments. Note that in some cases these structures are not unambiguous. For example, the metal methoxides CH_3OM^+ may also exist as hydrido–formaldehyde complexes $HM(OCH_2)^+$;[14,16] nor, of course, can agostic interactions be excluded. Nevertheless, irrespective of the actual ionic structures, all products can be explained in terms of the four generalized pathways defined in Scheme 1. A plausible reaction network, based on experiments with the isotopologues of dimethyl peroxide, is given in Scheme 2.



Scheme 2.

Oxygen Atom Transfer: The early transition-metal ions Sc^+, Y^+, La^+, Ti^+, Zr^+, Hf^+ and Ta^+ yielded the oxocation MO^+ as the only ionic product in their reactions with dimethyl peroxide; for V^+, Nb^+ and W^+ additional products resulting from other pathways were observed as well. The structures of the corresponding neutral C_2H_6O product(s) could not be determined in our experimental setup. Enthalpic considerations would favour the elimination of dimethyl ether, for example by a four-centre process from **1**, as the most exothermic process.[17] However, due to the high dissociation energies of the newly formed metal–oxygen bond ($BDE(M^+-O) \geq 126\,kcal\,mol^{-1}$ for all metals discussed here; see Table 2),[18] consecutive losses of CH_4 and CH_2O and even of a methoxy and a methyl radical (see Scheme 2) are also thermochemically conceivable. Because of their high $M-O^+$ bond dissociation energies, further oxidation reactions with these metal oxides are impossible on thermochemical grounds.[18a, 19] Consequently, a metal-mediated oxygen transfer from a peroxide to an organic substrate cannot be accomplished with these early transition metals. In addition to the generation of the oxocation, formation of a metal hydroxide MOH^+ was observed to some extent for Nb^+, Mo^+ and W^+. There are several mechanistic scenarios conceivable for the production of MOH^+, and those involving an intracomplex hydrogen-atom abstraction by MO^+ from a loosely bound methoxy group or a four-centre hydrogen ion transfer in CH_3OMO^+ to generate CH_2O and MOH^+ are quite appealing.

Radical Losses: The first-row transition metals V^+–Ni^+ and Zn^+, as well as Mo^+ as the only member of the second row, formed the CH_3OM^+ species as the major product. As far as the genesis of this ion is concerned, on thermochemical grounds both loss of a methoxy radical from the initial insertion complex **1** or the consecutive liberation of a hydrogen atom and formaldehyde are possible, with the latter process being $22\,kcal\,mol^{-1}$ less exothermic. As already indicated, the resulting complexes may have equilibrating methoxy- and hydrido–formaldehyde structures, at least for some of the metal ions. Some insight into the genesis of these products was provided by the study of deuterated dimethyl peroxides. With a 1:2:1 mixture of $[D_0]$, $[D_3]$ and $[D_6]$ dimethyl peroxide as reactant, V^+ and Mn^+ yielded exclusively the isotopically pure complexes CH_3OM^+ and CD_3OM^+ in a 1:1 ratio. This finding is in line with a methoxy loss from **1** without prior activation of the β-hydrogen bonds. However, for Cr^+, Fe^+–$Ni^{\bullet}$ and Zn^+, partially H/D-equilibrated products $CH_{3-n}D_nOM^+$ ($n = 1, 2$) were observed in addition to CH_3OM^+ and CD_3OM^+. Although only qualitative conclusions can be drawn from the ratio of the isotopologues, this result clearly demonstrates that activation of the C–H/C–D bonds in both methoxy groups must precede the radical loss for these metals. One is tempted to invoke the dihydrido bisformaldehyde complex **2**, which is accessible from the initial insertion product **1** by two subsequent, reversible β-hydrogen shifts involving either methoxy group, as a possible reactive intermediate. Of course, this explanation cannot hold true for Zn^+, since in its ground state Zn^+ is not able to form more than one covalent bond, which rules out the existence of a high-valent intermediate like **2**.

In contrast to its neighbours within the periodic table, Cu^+ formed a formaldehyde–methoxy complex by loss of a hydrogen radical. Similarly, in the reaction of the 4d metal Cd^+ with dimethyl peroxide, formation of $(CH_2O)CdOCH_3^+$ was in fact the only observable process. The preferential loss of a hydrogen instead of a methoxy radical for these two metals can be understood in terms of kinetic effects[20] and thermodynamics. A longer lifetime of the initial intermediate should favour the cleavage of a $H-CH_2O^{\bullet}$ bond combined with the formation of a metal–formaldehyde complex as the more exothermic process as compared to the expulsion of a $CH_3O^{\bullet}$ radical.

In general, the second- and third-row transition metals are known to activate C–H bonds more readily than their lighter congeners.[21] Accordingly, the internal energy of the primary product CH_3OM^+ ions formed by methoxy radical loss in such cases is sufficient to bring about further elimination of dihydrogen resulting in hydrido–carbonyl complexes $(CO)MH^+$ or the isomeric formyl complexes $M(CHO)^+$. These sequential reactions were observed for the second-row transition metals Nb^+–Pd^+ and for W^+ and Ir^+. Finally, the genesis of the monohydrides ReH^+ and IrH^+ can be explained either as subsequent loss of carbon monoxide from $(CO)MH^+$ or, alternatively, as the elimination of formaldehyde from the methoxy complex.

Intramolecular Redox Reactions: The most prominent product among the third class of reactions, the metal-mediated disproportionation of CH_3OOCH_3, corresponds to the generation of the formaldehyde complex $(CH_2O)M^+$ and this species is observed for Cr^+, Fe^+–Cu^+, Nb^+–Ag^+, W^+ and Au^+. As indicated in Scheme 2, this product may be formed from **1** by a β-hydride shift to the metal ion followed by reductive elimination of methanol or, as an alternative, the consecutive losses of dihydrogen and formaldehyde. The third scenario, loss of a hydrogen and a methoxy radical, represents an endothermic process and can therefore be excluded. The outstanding reactivity of the Cu^+ cation was once more demonstrated in that a bisformaldehyde complex, $(CH_2O)_2Cu^+$, was the main product. The labelling experiments indicated that in the Cu^+ system the dihydrogen molecule is eliminated from the dihydrido bisformaldehyde complex **2**, since in the reaction with $[1,1,1\text{-}D_3]$ dimethyl peroxide only the formation of $(CH_2O)Cu(CD_2O)^+$ was observed, with the loss of HD. Therefore, for M = Cu one can exclude reversible β-hydride shifts $\mathbf{1} \rightleftharpoons \mathbf{2}$ (Scheme 2) preceding the reductive elimination of dihydrogen.

Not surprisingly, additional dehydrogenation of the $(CH_2O)M^+$ complexes was observed for the second- and third-row transition metals, resulting in carbonyl complexes $M(CO)^+$ for Nb^+, Ru^+–Pd^+, W^+, Ir^+, Pt^+ and Au^+. The two last metal ions also formed the dihydrogen complexes MH_2^+ as a complementary product in comparable amounts, and it is tempting to suggest that both products stem from a common intermediate, $H_2M(CO)^+$, which itself results from double C–H bond activation of a formaldehyde ligand.[22] If this holds true, it follows that $BDE(M^+-CO) \approx BDE(M^+-H_2)$ for M = Pt and Au. In the exchange reaction with deuterium, AuH_2^+ yielded the dideuterium complex AuD_2^+ as the only product, thus supporting a dihydrogen structure $Au(H_2)^+$. However, this experiment does not exclude a dihydride structure, if the collision complex with D_2 induces reductive elimination of H_2 without participation of a tetrahydride intermediate [Eq. (1)].

$$\begin{aligned} D_2 + M(H)_2^+ &\longrightarrow (D_2)M(H)_2^+ \\ &\rightleftharpoons (D_2)M(H_2)^+ \longrightarrow (D)_2M(H_2)^+\ (D)_2M^+ + H_2 \end{aligned} \tag{1}$$

For the corresponding platinum complex, about 10% $PtHD^+$ was observed. This concurs with an equilibrium $Pt(H_2)^+ \rightleftharpoons Pt(H)_2^+$, or a small activation barrier for the formation of a dihydrido species from the dihydrogen complex of Pt^+, which can be attributed to the different electronic ground states of Pt^+ (s^0d^9) and Au^+ (s^0d^{10}). For Rh^+, too, the mixed carbonyl–formaldehyde complex $(CH_2O)RhCO^+$ was observed as a minor product; this can be explained by two consecutive eliminations of dihydrogen.

Electron Transfer: Energetically, single electron transfer (SET) and the concomitant formation of $C_2H_6O_2^+$ is only possible if the ionization energy (IE) of the metal exceeds that of dimethyl peroxide, that is IE(M)$\geq$9.1 eV.[17] Note, however, that electron transfer did not occur with Ir^+, which possesses an IE of 9.1 eV. Provided that the charge exchange is not hampered by a barrier, for example because of differences in ion-dipole forces, this finding indicates that the actual IE of dimethyl peroxide might be higher than the value cited in the literature. In the present series of experiments, electron transfer from CH_3OOCH_3 to M^+ was only observed for the metal ions of the tenth group Zn^+ and Hg^+, which possess IEs of 9.4 and 10.4 eV, respectively. With respect to Zn^+, the observed products $CH_{3-n}D_nOZn^+$ ($n = 1$, 2, see above) can also be explained by assuming an initial SET from the peroxide to the metal cation followed by H/D exchange between both methoxy groups in the resulting dimethyl peroxide radical cation, which is loosely bound to the zinc atom;[23] the reaction may then be completed by SET from Zn to the organic ligand and a collapse of the complex to the observed products. We note in passing that, in contrast to the reactions (i)-(iii), the electron transfer (reaction iv) is not likely to correspond to an inner sphere process, that is, to proceed by the insertion intermediate **1**. More probably, an outer sphere electron transfer is operative.

Trends Across the Periodic Table: Most of the reactions of metal cations with dimethyl peroxide discussed here can be assumed to proceed via a common initial intermediate, the rovibrationally excited bismethoxide cation **1**. Therefore, the dissociation energies of the two newly formed M^+-OCH_3 bonds determine the exothermicity of the insertion step, and, as a consequence, the internal energy content of **1** will affect its further reactions. Unfortunately, reliable thermochemical data for cationic methoxy complexes are not yet available; to a first approximation we will use the dissociation energies of M^+-OH[24] and M^+-O[18] in order to investigate the influence of the excess energy of **1** on its reactivity. Figure 1 shows an overview of the relative contributions of the four processes described in the foregoing sections for all d-block metals studied here. With respect to the first-row transition metals, it is obvious that only the early oxophilic elements undergo oxygen-atom transfer, because of the high bond dissociation energies of the corresponding metal oxides (Table 2). As this reaction does not occur for metals with an M^+-O bond dissociation energy of less than 126 kcal mol^{-1}, this value can be regarded as the *conditio sine qua non* for oxygen transfer from dimethyl peroxide to a "naked" transition-metal cation.[25]

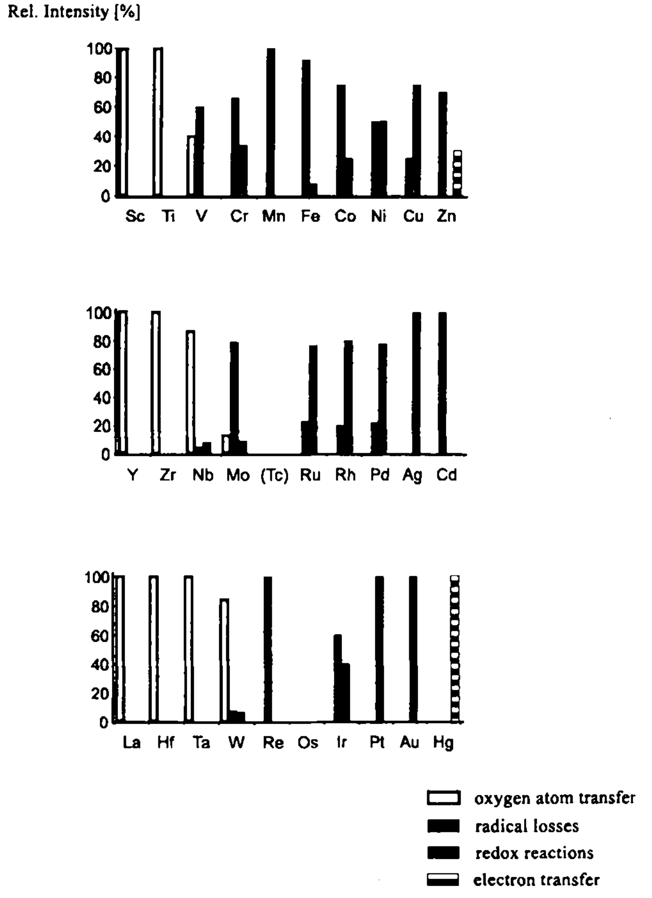


Fig. 1. Schematic representation of the product distribution (Scheme 1) in the reactions of M^+ with CH_3OOCH_3.

Table 2. Experimental bond dissociation energies (kcal mol^{-1}) of diatomic transition-metal oxide cations [a].

	BDE		BDE		BDE
ScO^+	164±2	YO^+	170± 5	LaO^+	206± 4
TiO^+	159±2	ZrO^+	201± 8	HfO^+	173± 5
VO^+	134±2	NbO^+	207±53	TaO^+	188±15
CrO^+	86±3	MoO^+	113±19	WO^+	126±10
MnO^+	68±3	TcO^+	–	ReO^+	–
FeO^+	81±2	RuO^+	93±10	OsO^+	100±12
CoO^+	77±2	RhO^+	55±10	IrO^+	59 –
NiO^+	63±2	PdO^+	49 –	PtO^+	59± 7
CuO^+	37±3	AgO^+	–	AuO^+	–
ZnO^+	38±3	CdO^+	–	HgO^+	–

[a] Taken from ref. [19].

The necessary condition to bring about electron transfer, the least common type of reaction in this study, is evident: atomic zinc and mercury exhibit closed-shell s^2d^{10} ground-state configurations,[26] resulting in relatively high first ionization energies of 9.4 and 10.4 eV to generate the corresponding monocations. As the IE of dimethyl peroxide is only 9.1 eV, SET from CH_3OOCH_3 to the ion to generate the neutral zinc or mercury atom can take place.

In contrast to the clear-cut pattern for oxygen-atom and electron transfer, it is much harder to find a comparable ordering principle for the radical losses and intramolecular redox reactions reflecting the electronic properties of the transition-metal ions. However, both processes start from the same intermediate, **1**, and, therefore, may be regarded as competing reaction paths. Entropically, the homolytic cleavage of a covalent bond resulting in the loss of a radical is favoured at high internal energies as compared to a rearrangement process; the latter has to precede the redox reaction. Accordingly, the internal energy of the insertion complex **1** will heavily affect the ratio of redox versus radical processes. In a first approximation, the higher the internal energy of **1**, the larger is the proportion of radical loss. As already mentioned, the excess energy depends on the M^+-OR bond dissociation energies, which can be approximated by that of the corresponding metal hydroxide cations MOH^+.

In Figure 2 we plot the bond energies M^+-OH and the relative intensities of total radical losses for the 3d cations V^+–Cu^+; with the exception of V^+ the assumed relation seems to be valid in that large M^+-OH bond energies result in the preferred expulsion of radicals. The anomalous behaviour of V^+ (i.e., the relatively small proportion of radical loss and a high BDE(V^+-OH)) does not actually contradict our working model in that, owing to its very large BDE, the resulting CH_3OV^+ is still so

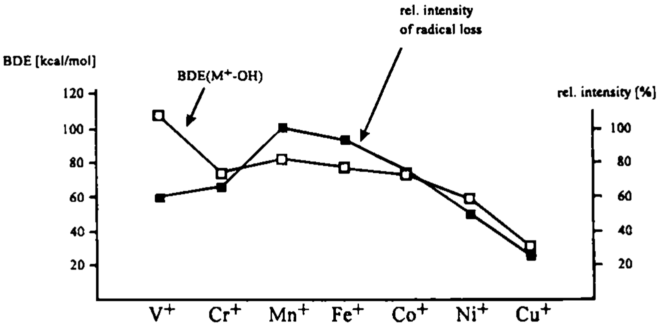


Fig. 2. Relative intensities of radical loss and M–OH$^+$ bond dissociation energies for M$^+$ = V$^+$–Cu$^+$. Open squares correspond to BDEs and solid squares to the intensities of total radical loss.

energetic that it will further decompose to VO$^+$ and CH$_3^\bullet$. For the two extreme cases, Mn$^+$ and Cu$^+$, the correlation works well: manganese, with BDE(Mn$^+$–OH) = 81 kcal mol^{-1}, does indeed exhibit the loss of CH$_3$O$^\bullet$ as the only reaction, while copper (BDE(Cu$^+$–OH) = 30 kcal mol^{-1})[27] represents the minimum in yielding only 25% open-shell neutrals.

Although the electronic ground-state configuration of the metal ions is already reflected in the M$^+$–OH bond energies, a closer inspection of the electronic situation may provide a further clue as to the origin of the observed products. For example, chromium and iron possess nearly equal M$^+$–OH bond energies and yet the radical loss is much less marked for chromium (66% and 93%, respectively). This finding can be ascribed to the s^{0}d^5 ground-state configuration of Cr$^+$, which favours donor-type bonding to the empty s orbital as provided by a closed-shell ligand like formaldehyde, leaving the half-filled d^5 shell more or less unperturbed. In contrast, Fe$^+$ with its s^{1}d^6 configuration favours a covalently bound ligand, such that radical loss is encouraged. Similarly, the high selectivity of manganese for radical loss may also be explained by its s^{1}d^5 configuration, which promotes the formation of exactly one single covalent bond to an open-shell ligand involving the 4s orbital. The same explanation may be adopted to Zn$^+$ (s^{1}d^{10}), which does not undergo the intramolecular redox reaction; rather, loss of a methoxy radical is the only process which can compete with electron transfer.

A detailed correlation of product formation versus electronic structure such as that for the first-row transition metals above is not yet available for the heavier elements. Nevertheless, in the comparison of the 3d versus 4d and 5d block transition-metal cations, a few general trends emerge. We note that the large M$^+$–O bond energies of Y$^+$, Zr$^+$, Nb$^+$, La$^+$, Hf$^+$, Ta$^+$ and W$^+$ result in the preferred, if not exclusive, formation of MO$^+$. Further, the large IE of 10.4 eV for Hg is reflected in a quantitative electron transfer to generate CH$_3$OOCH$_3^{+\bullet}$ from the reaction of Hg$^+$ with CH$_3$OOCH$_3$. Eventually, the intensity of radical losses decreases upon going down from the first row, whereas the intramolecular redox reactions gain in importance. While only one covalent bond is broken in the radical loss, hydrogen rearrangements must occur in the redox reaction. As the predominant d character of the metal orbitals of second- and third-row metals provides a better overlap with the hydrogen s orbital, we would expect the barrier for β-H shifts to be lower for the heavier metal ions.[28] In contrast to this general trend, however, an exclusively radical-type reaction was observed for the fifth group member rhenium, resulting in the formation of ReH$^+$. Again, this finding is in keeping with the s^{1}d^5 electronic ground-state configuration of the rhenium cation, which favours a single covalent bond. Unfortunately, a correlation between bond energies[29] and the distribution of the radical and redox processes, as given above for the first-row transition metals, cannot be found for the second and third row. For example, ruthenium, rhodium and palladium show almost identical ratios of both processes in spite of the fact that the corresponding bond energies are significantly different (Table 2). On the other hand, platinum and iridium exhibit the same experimental M$^+$–O bond energies, but quite different reactivities. Obviously, many factors influence the reactivities of the heavy transition metals leading to a by and large unique behaviour for each element. A simplified picture, as given above for the first-row transition metals, is not yet available to explain the experimental results for the higher congeners; in addition to the effects of overlap and electronic ground-state features, relativistic effects may cause this irregularity,[30] and further work, both experimental and theoretical, is required to resolve these intricate effects.

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