149. Intermediacy of Proton-Bound Dimers and Ion/Dipole Complexes in the Unimolecular Decompositions of Dialkyl-Peroxide Radical Cations: Evidence for a Coupled Proton and Hydrogen-Atom Transfer

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The unimolecular fragmentation reactions of the radical cations of diethyl, diisopropyl, dipropyl, isopropyl propyl, and di(*tert*-butyl) peroxide have been investigated by mass spectrometric and isotopic labeling techniques. Two competing pathways for unimolecular decomposition in the μs time regime (metastable ions) are observed: *i*) A combination of an α-C–C bond cleavage and a H migration gives rise to proton-bound dimers of two ketone or aldehyde molecules. *ii*) Ion/dipole complexes of alkyl cations and alkylperoxy radicals are generated by C–O bond cleavage. These complexes either exhibit direct losses of alkylperoxy radicals, or they rearrange *via* a coupled proton and H-atom transfer, this sequence of unprecedented isomerizations is completed by losses of alkyl radicals. Collisional activation experiments confirm that the ionic products of the latter process correspond to $RR'C{=}OOH^+$; these ions can be regarded as protonated carbonyl oxides. In addition, we observe the elimination of alkenes leading to hydroperoxide radical cations and the expulsion of $HO_2^·$ radicals. The latter process implies a C–C bond formation step between the two alkyl fragments leading to higher alkyl cations.

Introduction. – Although the mass-spectrometric behavior of most classes of organic compounds has been the subject of numerous investigations, systematic mass-spectrometric studies of dialkyl-peroxide radical cations are scarce [1]. Peroxides have mostly been studies in the context of structural analysis¹), and detailed investigations of mechanistic pathways for the unimolecular decompositions of peroxide-radical cations applying isotopic labeling have only rarely been performed [3] [4]. As far as the structures of the peroxides are concerned, mass-spectrometric experiments have been conducted predominantly on the thermally quite stable tertiary dialkyl peroxides [5], while simple primary and secondary dialkyl peroxides have almost completely been neglected so far²).

Here, we describe a general reaction scheme for the unimolecular decomposition of peroxide radical cations $\mathbf{1}^{+·}$–$\mathbf{5}^{+·}$ as obtained by a combination of isotopic-labeling techniques and mass-spectrometric means. The variety of products is discussed in terms of two competing fragmentation pathways, and evidence is presented for the intermediacy of proton-bound dimers and ion/dipole complexes [7]. These studies uncover an unprecedented coupled proton-transfer and hydrogen-migration process giving rise to protonated carbonyl oxides. These '*Criegee* intermediates' are believed to play an important role in the reaction of O_3 with olefins [8].

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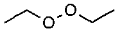
¹) For an application of nine different ionization techniques in the structural analysis of organic peroxides, see [2].

²) For a combined mass-spectrometric and computational analysis of the unimolecular decompositions of $CH_3OOCH_3^{+·}$, see [6].



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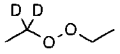

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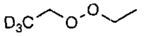

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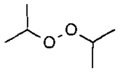

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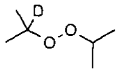

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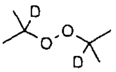

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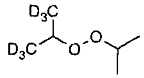

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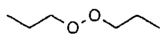

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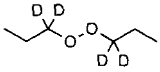

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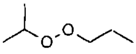

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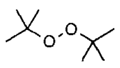

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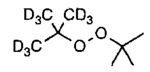

5a

Experimental. – The experiments were performed with a modified *VG ZAB/HF/AMD* four-sector mass spectrometer of *BEBE* configuration (*B* stands for magnetic and *E* for electric sectors), which has been described in [9]. Briefly, the peroxides were ionized in an electron impact (EI) source by a beam of electrons having 70 eV kinetic energy. To avoid thermal peroxide decomposition, a metal-free *Teflon*/glass inlet system was used. The ions were accelerated to 8 keV translational energy and mass-selected by means of $B(1)/E(1)$ at a resolution of $m/\Delta m = 3{,}000$. 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, mass-selected ions were collided with He (80% transmission (T)). The error of the relative intensities in MS/MS experiments does not exceed ±5%. MS/MS/MS Experiments [10] were performed by selecting the primary 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. On principal grounds, the sensitivity in MS/MS/MS experiments is less than that of the MS/MS studies, and the error is estimated to ±15%. All spectra were accumulated and on-line processed with the *AMD-Intectra* data system; 5 to 30 scans were averaged to improve the signal-to-noise ratio. The syntheses of most of the peroxides have been reported in [11]. Dipropyl peroxides were prepared by reacting propyl bromide or [1,1-D_2]propyl bromide, respectively, with potassium superoxide under phase-transfer conditions [12]. Isopropyl propyl peroxide was synthesized by alkylation of isopropyl hydroperoxide with propyl bromide [13]. All substances were purified by distillation and characterized by their ^{1}H-NMR and EI mass spectra.

Results and Discussion. – The unimolecular fragmentation reactions of unlabeled $\mathbf{1}^{+\cdot}$–$\mathbf{5}^{+\cdot}$ are summarized in *Table 1*. The products can be classified into six categories: *i*) The isomeric dipropyl peroxides $\mathbf{2}^{+\cdot}$–$\mathbf{4}^{+\cdot}$ and di(*tert*-butyl) peroxide $\mathbf{5}^{+\cdot}$ reveal losses of a $CH_3^{\cdot}$ radical ($\Delta m = 15$) as the major neutral product. The eliminations of *ii*) alkenes ($\Delta m = 28$, 42), *iii*) alkyl radicals ($\Delta m = 29$, 43), and *iv*) $HO_2^{\cdot}$ radicals ($\Delta m = 33$) are observed for diethyl and dipropyl peroxides $\mathbf{1}^{+\cdot}$–$\mathbf{4}^{+\cdot}$. Finally, *v*) signals for protonated carbonyl compounds ($\Delta m = 59$, 73, 87) and *vi*) alkyl cations ($\Delta m = 75$, 89) are present in the MI mass spectra of $\mathbf{2}^{+\cdot}$–$\mathbf{5}^{+\cdot}$. The latter process is observed also in the MI spectrum of $\mathbf{1}^{+\cdot}$, but the intensity is much less than 1%. The relative intensities observed in the MI mass spectra of $\mathbf{1}^{+\cdot}$–$\mathbf{5}^{+\cdot}$ depend on the structure of the peroxides, and the aim of the present investigation is to provide a plausible explanation. The by far most intense process in the MI spectrum of diethyl peroxide $\mathbf{1}^{+\cdot}$ is the expulsion of ethene, while di(*tert*-butyl) peroxide $\mathbf{5}^{+\cdot}$ exhibits two major peaks corresponding to the losses of $CH_3^\cdot$ and *t*-BuOO·. The other processes are weak or even absent for $\mathbf{1}^{+\cdot}$ and $\mathbf{5}^{+\cdot}$. However, in the MI spectra of diisopropyl peroxide $\mathbf{2}^{+\cdot}$ all reactions are present, and, therefore, in the following we will first focus on the unimolecular decay of $\mathbf{2}^{+\cdot}$. A general mechanistic scheme will be presented, and the similarity of the spectra of $\mathbf{2}^{+\cdot}$–$\mathbf{4}^{+\cdot}$ is explained in terms of an isomerization process $\mathbf{3}^{+\cdot} \rightarrow \mathbf{4}^{+\cdot} \rightarrow \mathbf{2}^{+\cdot}$. Finally, the mass-spectral differences of $\mathbf{2}^{+\cdot}$–$\mathbf{4}^{+\cdot}$, as compared to $\mathbf{1}^{+\cdot}$ and $\mathbf{5}^{+\cdot}$, are traced back to structural features and reaction energetics. Before doing so, we note, in passing, in agreement with theoretical and experimental results [6] obtained for ionized CH_3OOCH_3, that the peroxide cation radicals most likely have the connectivity of the neutral peroxides. Thus, it is justified to use the peroxidic structures of $\mathbf{1}^{+\cdot}$–$\mathbf{5}^{+\cdot}$ as starting points for the discussion of their unimolecular decays.

Table 1. *Mass Differences* (Δm in amu) *Observed in the MI Mass Spectra of the Molecular Ions* ($M^{+\cdot}$) *of Dialkyl Peroxides* $\mathbf{1}^{+\cdot}$–$\mathbf{5}^{+\cdot}$[a])

	$M^{+\cdot}$	Δm										
	m/z	−15	−28	−29	−33	−42	−43	−59	−73	−75	−87	−89
$\mathbf{1}^{+\cdot}$	90		88	8	4							
$\mathbf{2}^{+\cdot}$	118	56			1	3	16	21	1	2		
$\mathbf{3}^{+\cdot}$	118	45			10	15	13	15	1	1		
$\mathbf{4}^{+\cdot}$	118	50			7	8	14	18	1	2		
$\mathbf{5}^{+\cdot}$	146	76							1		3	18

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

In the unimolecular fragmentation reactions of $\mathbf{2}^{+\cdot}$, the loss of a methyl radical ($\Delta m = 15$) corresponds to the major process. It involves an intact CH_3 group from the β-position, as indicated by the data of labeled $\mathbf{2a}^{+\cdot}$–$\mathbf{2c}^{+\cdot}$ (*Table 2*). The ratio of $CH_3^\cdot$ ($\Delta m = 15$) and $CD_3^\cdot$ ($\Delta m = 18$) radicals expelled from $\mathbf{2c}^{+\cdot}$ indicates the operation of a significant secondary kinetic isotope effect (KIE) of 1.18 per D. The ionic products of methyl losses have been characterized by MI/CA experiments in which three closely related processes are observed: the base peak corresponds to a mass difference of $\Delta m = 44$, most likely due to the loss of neutral acetaldehyde concomitant with the formation of protonated acetone. *Vice versa*, the expulsion of acetone ($\Delta m = 58$) leads to protonated acetaldehyde; this ion is generated with much lower intensity (4% relative to the base peak) due to the lower proton affinity (PA) of acetaldehyde ($PA = 186.6$ kcal/mol)[3]) as compared to that of acetone ($PA = 196.7$ kcal/mol [14a]; 193.7 kcal/mol [14b]). As a minor reaction, the acetyl cation (5%) contributes to the MI/CA spectra. These findings are typical for proton-bound dimers of carbonyl compounds [15][4]). Therefore, the structure of the daughter ions corresponding to methyl loss from $\mathbf{2}^{+\cdot}$ can be formulated as a proton-bound dimer of acetaldehyde and acetone. In addition, these MI/CA results further imply that the presence of signals for protonated acetone

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[3]) Proton affinities are taken from [14]. For a recent value of PA(acetone), see [14b].

[4]) For a semi-empirical study on the proton-bound dimer of acetone, see [15e].

Table 2. *Mass Differences* (*Δm* in amu) *Observed in the MI Mass Spectra of* $[C_6,H_{14},O_2]^{+\cdot}$ *Ions* $\mathbf{2}^{+\cdot}$–$\mathbf{4}^{+\cdot}$ *and the Corresponding Isotopologues*[a])

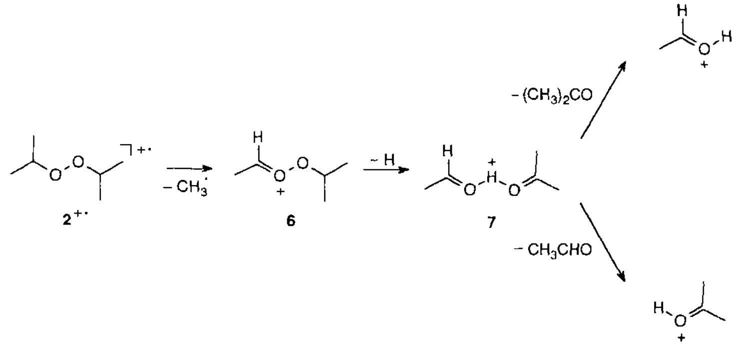
	Δm											
	−15	−16	−17	−18	−33	−34	−42	−43	−44	−45	−47	−48
$\mathbf{2}^{+\cdot}$	56				1		3	16				
$\mathbf{2a}^{+\cdot}$	44				1		2	2	18			
$\mathbf{2b}^{+\cdot}$	50				1			3		19		
$\mathbf{2c}^{+\cdot}$	29			11	1	1	3	13			2	9
$\mathbf{3}^{+\cdot}$	45				10		15	13				
$\mathbf{3a}^{+\cdot}$	21	5	18		7	3		6	15	8		
$\mathbf{4}^{+\cdot}$	50				7		8	14				

	Δm										
	−59	−60	−61	−65	−73	−74	−75	−76	−77	−79	−81
$\mathbf{2}^{+\cdot}$	21				1		2				
$\mathbf{2a}^{+\cdot}$	12	15			2	2	1	1			
$\mathbf{2b}^{+\cdot}$		23				3		1			
$\mathbf{2c}^{+\cdot}$	14			11			1	2		2	1
$\mathbf{3}^{+\cdot}$	15				1		1				
$\mathbf{3a}^{+\cdot}$			15				1		1		
$\mathbf{4}^{+\cdot}$	18				1		2				

[a]) Intensities are normalized to Σ reactions = 100%. Intensities less than 1% are omitted.

(*Δm* = 59) and protonated acetaldehyde (*Δm* = 73) in the MI mass spectra of $\mathbf{2}^{+\cdot}$ (*Table 1*) may be attributed to consecutive losses of a methyl radical and the corresponding carbonyl compound. The structural assignment and the assumption of a consecutive reaction leading to the protonated carbonyls are in line with the data obtained for labeled $\mathbf{2a}^{+\cdot}$–$\mathbf{2c}^{+\cdot}$; further, the CA mass spectrum of the independently generated proton-bound dimer of acetone and acetaldehyde **7** is identical with that of the ion $[\mathbf{2} - CH_3]^+$. A mechanistic scenario is depicted in *Scheme 1*, and, assuming that the methyl loss represents a simple cleavage of an α-C–C bond in the structurally intact peroxide radical cation, the intermediate **6** is formed, which subsequently rearranges *via* a H shift to the proton-bound dimer **7**.

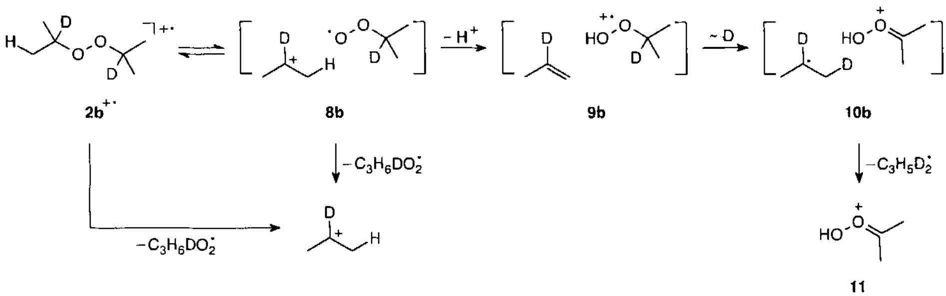
Scheme 1



As far as the formation of propyl cations ($\Delta m = 75$) from $\mathbf{2}^{+\cdot}$ and the seemingly complementary losses of propyl radicals ($\Delta m = 43$) are concerned, the label distribution as obtained for $\mathbf{2a}^{+\cdot}$–$\mathbf{2c}^{+\cdot}$ (*Table 2*) is quite revealing. In the propyl cations, the number of D-atoms incorporated is not unexpected: we observe [D_0]- and [D_1]propyl$^+$ ($\Delta m = 76, 75$) from $\mathbf{2a}^{+\cdot}$, [D_1]propyl$^+$ ($\Delta m = 76$) from $\mathbf{2b}^{+\cdot}$, and [D_0]- and [D_6]propyl$^+$ ($\Delta m = 81, 75$) from $\mathbf{2c}^{+\cdot}$. In contrast, the isotope distribution associated with the elimination of the propyl radicals is quite surprising, because *both* α-H-atoms of the peroxy C-atoms are incorporated in the propyl radical formed from $\mathbf{2}^{+\cdot}$. This follows from the occurrence of exclusive losses of $C_3H_6D^\cdot$ ($\Delta m = 44$) from $\mathbf{2a}^{+\cdot}$ and $C_3H_5D_2^\cdot$ ($\Delta m = 45$) from $\mathbf{2b}^{+\cdot}$. Further insight into the reaction mechanism is gained from the finding that [D_6]-labeled $\mathbf{2c}^{+\cdot}$ forms $C_3H_7^\cdot$ and $C_3H_2D_5^\cdot$ ($\Delta m = 43, 48$) instead of $C_3HD_6^\cdot$ ($\Delta m = 49$). Obviously, two H-atoms from different alkyl chains are transferred in the course of propyl-radical losses. Two additional arguments further support the assumption that propyl radicals are formed *via* a rearrangement process, while the formation of $C_3H_7^+$ is due to a simple C–O bond cleavage: *i*) the ionization energy (*IE*) of isopropylperoxy radicals ($IE \approx 11$ eV[5])[6]) is much higher than that of i-$C_3H_7^\cdot$ ($IE = 7.37$ eV). Thus, on thermochemical grounds cleavage of a C–O bond in $\mathbf{2}^{+\cdot}$ leads directly to isopropyl cations and isopropylperoxy radicals, in agreement with the isotope distribution for the propyl cations. *ii*) Upon collisional activation, one would expect that a simple bond-cleavage process gains in intensity at the expense of rearrangements. Indeed, in the CA mass spectrum of $\mathbf{2}^{+\cdot}$ the intensities of $C_3H_7^+$ and the ionic product due to the loss of neutral $C_3H_7^\cdot$ are more or less comparable, while in the MI spectrum of $\mathbf{2}^{+\cdot}$, the $C_3H_7^+$ ($\Delta m = 75$) signal is *ca.* 16 times less intense as compared to the expulsion of $C_3H_7^\cdot$ ($\Delta m = 43$).

The mechanism depicted in *Scheme 2* for the radical cation $\mathbf{2b}^{+\cdot}$ provides a rationalization for these observations. The first step, $\mathbf{2b}^{+\cdot} \rightarrow \mathbf{8b}$, corresponds to a C–O bond cleavage, which gives rise to the ion/dipole complex **8b**, in which an isopropylperoxy radical and a propyl cation are held together by electrostatic forces. Formation of similar ion/dipole complexes [7] [17] have been reported in a variety of open- [18] and closed-shell [19] O- and N-containing compounds and were invoked to explain the observed fragmentation patterns. From $\mathbf{2b}^{+\cdot}$, $C_3H_6D^+$ ions arise, if the peroxy radical is lost either directly from the molecular ion or from intermediate **8b**. In competition, **8b** may undergo a

Scheme 2



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[5] The *IE*s of alkylperoxy radicals were estimated on the basis of $IE(OH_2^\cdot) = 11.35$ eV [16].

[6] If not stated otherwise, *IE*s and thermochemical data were taken from [16].

proton transfer from the acidic methyl group of the carbocation building block to the peroxy radical to yield **9b** as a second ion/dipole complex; this species further rearranges thus leading to **10b** *via* transfer of the α-D-atom of the hydroperoxide moiety. Thus, in line with the experimental findings, these coupled proton and hydrogen-atom transfers lead to the expulsion of the $C_3H_5D_2^{\cdot}$ radical and **11** as the ionic product.

Ion **11** itself is interesting, since it can be regarded as a protonated carbonyl oxide, which figures in the literature as '*Criegee* intermediate' [8]. We have succeeded in structurally characterizing **11** by MI/CA experiments (*Table 3*). Upon collisional activation, three major processes are observed. Losses of an $OH^{\cdot}$ radical, water ($\Delta m = 17, 18$) and 'methanol' ($\Delta m = 32$); the latter process constitutes a combination of $OH^{\cdot}$ and $CH_3^{\cdot}$ eliminations, rather than the elimination of genuine CH_3OH. The CA data are completely in line with the proposed structure of **11**. Further, the isotopic-labeling experiments support the structural assignment and, additionally, uncover mechanistic features of the formation of **11**. For example, in the MI/CA mass spectrum of $[\mathbf{2c} - 48]^+$ signals due to losses of $OD^{\cdot}$, HDO, and 'CH_3OD' ($\Delta m = 18, 19$, and 33, resp.) are observed, confirming that the D-atom originating from a methyl group is indeed transferred to the O-atom of the peroxy radical in the protonation step.

Table 3. *Mass Differences* (Δm in amu) *Observed in the MI/CA Spectra of Ions Generated from* $\mathbf{2}^{+\cdot}$–$\mathbf{4}^{+\cdot}$ *by Losses of Isotopologous Propyl Radicals*[a]

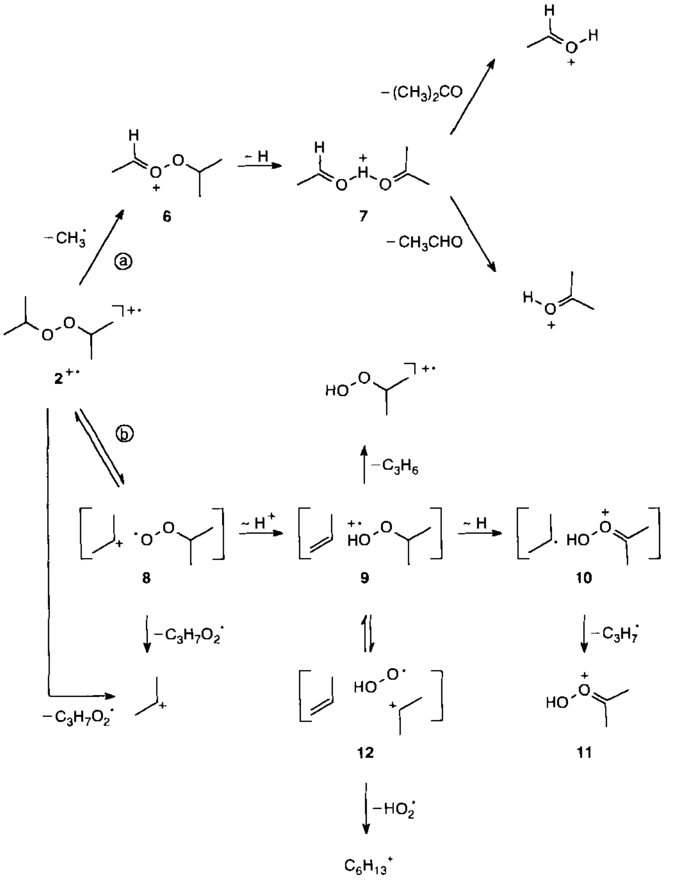
	Δm					
	−17	−18	−19	−32	−33	−35
$[\mathbf{2} - 43]^+$	100	15		40		
$[\mathbf{2a} - 44]^+$	100	13		38		
$[\mathbf{2b} - 45]^+$	100	16		41		
$[\mathbf{2c} - 43]^+$	100		18			51
$[\mathbf{2c} - 48]^+$		100	16		38	

[a] Intensities are given relative to the base peak = 100%. Some minor processes are omitted.

Two minor reactions of $\mathbf{2}^{+\cdot}$ have not yet been adressed, namely the losses of propene ($\Delta m = 42$) and $HO_2^{\cdot}$ ($\Delta m = 33$). *Scheme 3* summarizes the fragmentation mechanisms of $\mathbf{2}^{+\cdot}$ discussed so far and, in addition, gives a plausible rationalization for these two processes: *i*) after the proton transfer **8** → **9**, the ion/dipole complex **9** may dissociate *via* expulsion of propene to give rise to the radical cation of isopropyl hydroperoxide. Due to the low intensity of this signal, a structural characterization by MI/CA experiments could not be achieved. However, the assumption of a hydroperoxide structure seems to be plausible, since for the analogous ethene losses from $\mathbf{1}^{+\cdot}$ the ionic product has been identified as the ethyl-hydroperoxide radical cation (see below). *ii*) In analogy to step $\mathbf{2}^{+\cdot} \rightarrow \mathbf{8}$, a second C–O bond cleavage within **9** may lead to a loosely interacting cluster **12**. Loss of $HO_2^{\cdot}$ together with C–C bond formation leads to a hexyl cation as ionic product. Both mechanisms are in keeping with the isotope distributions obtained for $\mathbf{2a}^{+\cdot}$–$\mathbf{2c}^{+\cdot}$ (*Table 2*).

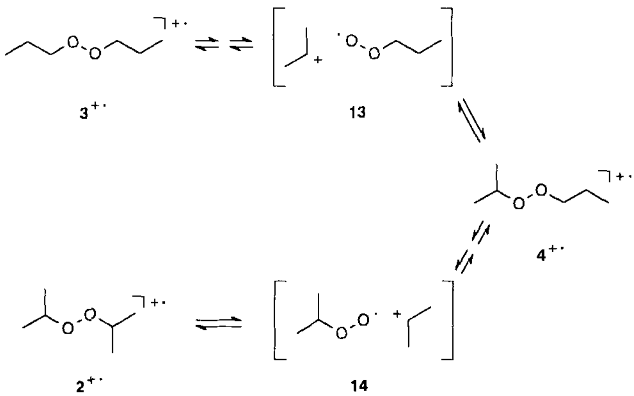
For the sake of clarity, we note in passing that *Scheme 3* is formulated exemplarily for $\mathbf{2}^{+\cdot}$. In the following sections, we will demonstrate that the same mechanistic pathways account for the decompositions of the other peroxide radical cations as well.

Scheme 3



A comparison of the MI mass spectra of $\mathbf{2}^{+\cdot}$–$\mathbf{4}^{+\cdot}$ radical cations reveals no qualitative differences (*Table 2*) in that processes observed for one of these ions are not found in the MI spectra of the others. Thus, the MI mass spectra are similar to each other, although the relative intensity patterns distinctly alter depending on the peroxide structure. However, the expulsion of $CH_3^{\cdot}$ radicals ($\Delta m = 15$) from $\mathbf{3}^{+\cdot}$ cannot easily be explained, if the radical cation had pertained the dipropyl-peroxide structure. Obviously, at least one of the propyl groups has to isomerize to isopropyl [19b], before a methyl radical is formed. In line with this interpretation (*Scheme 4*), two signals with nearly the same intensities are observed for the methyl losses, if the α-positions are completely deuterated ($\mathbf{3a}^{+\cdot}$), namely $CH_3^{\cdot}$ ($\Delta m = 15$) and $CHD_2^{\cdot}$ ($\Delta m = 17$; *Table 2*). A less intense peak for $CH_2D^{\cdot}$ indicates that a minor fraction of the ions participate in H/D-exchange processes within the propyl side chain. Similar arguments can be applied for the other processes in the MI mass spectra of $\mathbf{3a}^{+\cdot}$, and the isotope distribution can only be fully understood, if a

Scheme 4



propyl→isopropyl isomerization is operative. This rearrangement further confirms the proposed intermediacy of ion/dipole complexes such as **13** or **14** in the course of unimolecular decompositions of $\mathbf{2}^{+\cdot}$–$\mathbf{4}^{+\cdot}$ (*Scheme 4*).

However, $\mathbf{2}^{+\cdot}$ is not formed from all $\mathbf{3}^{+\cdot}$ and $\mathbf{4}^{+\cdot}$ ions, since then the MI mass spectra of $\mathbf{2}^{+\cdot}$–$\mathbf{4}^{+\cdot}$ would be expected to be more or less identical, which is not the case. Methyl losses from $\mathbf{3}^{+\cdot}$ and the consecutive formation of protonated carbonyl compounds (pathway ⓐ analogous to *Scheme 3*) are only attainable following the propyl→isopropyl isomerization. Thus channel ⓐ is only accessible for that fraction of $\mathbf{3}^{+\cdot}$, which already isomerized to $\mathbf{4}^{+\cdot}$ or $\mathbf{2}^{+\cdot}$. The intensity of the methyl losses from $\mathbf{3}^{+\cdot}$ should decrease reflecting that part of the ion population which does not undergo a rearrangement. In contrast, pathway ⓑ (in analogy to *Scheme 3*), for which no propyl→isopropyl rearrangement is mandatory, should be favored. Consequently, one expects that the intensities of methyl losses and the formation of protonated acetone decrease in the order $\mathbf{2}^{+\cdot} > \mathbf{4}^{+\cdot} > \mathbf{3}^{+\cdot}$, if the mechanistic pictures as given in *Schemes 3* and *4* hold true. *Vice versa*, the processes following path ⓑ should gain in intensity in the same sequence. This is indeed observed, with the exception of the propyl-radical losses, which do not change much in intensity. Here, thermochemical arguments may apply, since $CH_3CH_2CH{=}O{-}OH^+$ **15** should be formed from unrearranged $\mathbf{3}^{+\cdot}$ and $\mathbf{4}^{+\cdot}$ as well as **11** following rearrangement to $\mathbf{2}^{+\cdot}$. Due to the higher degree of alkyl substitution at the carbonyl C-atom **11** is more stabilized as compared to **15**.

In its unimolecular decay, diethyl peroxide $\mathbf{1}^{+\cdot}$ reveals three MI processes (*Table 4*): *i*) ethene loss ($\Delta m = 28$) leads to the formation of ethyl-hydroperoxide radical cations as the major reaction channel. The ionic product has been characterized by MI/CA experiments (*Table 5*). The MI/CA spectra reveal eliminations of $CH_3^{\cdot}$, $OH^{\cdot}$, the consecutive expulsion of $OH^{\cdot}$ and H_2, the formation of ethyl cations, and some other minor processes. A comparison of the MI/CA spectra to a CA mass spectrum of authentic ethyl hydroperoxide (*Table 5*) indicates that the product of ethene elimination from $\mathbf{1}^{+\cdot}$ corresponds indeed to the ethyl-hydroperoxide structure[7]). The data of isotopically labeled com-

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[7]) The intensity differences in the MI/CA spectrum of the $[\mathbf{1} - C_2H_4]^{+\cdot}$ ion and the CA spectrum of ionized ethyl hydroperoxide most likely are due to different internal-energy contents of these ions.

pounds are in line with this interpretation as well. *ii*) The loss of ethyl radicals ($\Delta m = 29$) is subject to a similar proton/hydrogen transfer mechanism as suggested for the formation of propyl radicals from $\mathbf{2}^{+\cdot}$. This can be deduced from the generation of $C_2H_3D_2^{\cdot}$ as neutral product from $\mathbf{1b}^{+\cdot}$ instead of $C_2H_2D_3^{\cdot}$. *iii*) Finally, the loss of $HO_2^{\cdot}$ is observed as well. Thus, all products observed in the MI mass spectra of $\mathbf{1}^{+\cdot}$ can be rationalized by a mechanism analogous to channel ⓑ in *Scheme 3*, while no products corresponding to pathway ⓐ are observed (see below).

Table 4. *Mass Differences* (Δm in amu) *Observed in the MI Mass Spectra of* $\mathbf{1}^{+\cdot}$–$\mathbf{1b}^{+\cdot}$[a])

	Δm					
	−28	−29	−30	−31	−33	−34
$\mathbf{1}^{+\cdot}$	88	8			4	
$\mathbf{1a}^{+\cdot}$	48	2	44	4	2	
$\mathbf{1b}^{+\cdot}$	54	7	32	4	2	1

[a]) Intensities are normalized to Σ reactions = 100%. Intensities less than 1% are omitted.

Table 5. *Mass Differences* (Δm in amu) *Observed in the MI/CA Spectra of Ions Generated from* $\mathbf{1}^{+\cdot}$–$\mathbf{1b}^{+\cdot}$ *by Losses of Isotopologous Ethenes*[a])

	Δm												
	−15	−17	−18	−19	−20	−21	−33	−34	−35	−36	−47	−48	−49
$[\mathbf{1} - 28]^{+\cdot}$	33	100		34			96	5	10		2		
$[\mathbf{1a} - 28]^{+\cdot}$	40	82				25	100	32	11	5			1
$[\mathbf{1a} - 30]^{+\cdot}$	34	89		36			100	5	11		1		
$[\mathbf{1b} - 28]^{+\cdot}$		82	48	39			100	3	15	18	3		
$[\mathbf{1b} - 30]^{+\cdot}$	41		85		42			100	4	12		2	
$C_2H_5OOH^{+\cdot}$[b])	15	100		13			44	4	6		2		

[a]) Intensities are given relative to the base peak = 100%. Some minor processes are omitted.

[b]) CA Mass spectrum of ethyl hydroperoxide generated independently from an authentic sample in the EI ion source.

In contrast, in the MI mass spectrum of $\mathbf{5}^{+\cdot}$ (*Table 6*) $CH_3^{\cdot}$ loss gives rise to the base peak. In contrast to $[\mathbf{2} - CH_3]^+$, the transfer of an α-H-atom to yield a proton-bound dimer is, on structural grounds, not feasible for $[\mathbf{5} - CH_3]^+$. The CH_3^+-bound bis-acetone structure, which would be analogous to **7** (*Scheme 3*), is expected to be much less stable as compared to the corresponding proton-bound intermediate, since the methyl-cation affinity (*MCA*) of acetone (*MCA* = 96 kcal/mol[8]) is much lower than the proton affinity (*PA* = 196.7 kcal/mol). This is confirmed by the MI/CA mass spectrum of $[\mathbf{5a} - CH_3]^+$ with losses of [D$_0$]acetone as the base peak, while no [D$_6$]acetone is eliminated. *Vice versa*, upon collisional activation $[\mathbf{5a} - CD_3]^+$ gives rise exclusively to [D$_6$]acetone as neutral product. Thus, for $\mathbf{5}^{+\cdot}$ we propose the methyl loss to be a simple α-cleavage process to give an ion similar to **6**; rearrangement to a symmetric ion analogous to **7** does not take place. The second prominent peak in the MI mass spectrum of $\mathbf{5}^{+\cdot}$ corresponds to the *tert*-butyl

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[8]) See, *e.g.*, the discussion of singlet and triplet CH_3O^+ cations in [20].

cation, which is formed by C—O bond cleavage and expulsion of a (*tert*-butyl)peroxy radical. However, the losses of isobutene, butyl radicals, or $HO_2^{\cdot}$ are not observed; most likely t-$C_4H_9^+$ serves as a sink such that all other possible pathways of sequence ⓑ are suppressed on energetic grounds (see below).

Table 6. *Mass Differences* (Δm in amu) *Observed in the MI Mass Spectra of* $\mathbf{5}^{+\cdot}$ *and* $\mathbf{5a}^{+\cdot}$ a)

	Δm								
	−15	−18	−73	−82	−87	−89	−90	−95	−98
$\mathbf{5}^{+\cdot}$	78		1		3	18			
$\mathbf{5a}^{+\cdot}$	38	23	1	1		11	2	2	22

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

In the foregoing sections, it has been shown that the unimolecular decompositions of $\mathbf{1}^{+\cdot}$–$\mathbf{5}^{+\cdot}$ can be rationalized by a general scheme, which is depicted in *Scheme 3* for $\mathbf{2}^{+\cdot}$. We should recall that $\mathbf{1}^{+\cdot}$ does not reveal products corresponding to channel ⓐ, while $\mathbf{5}^{+\cdot}$ does not react *via* an ion/dipole complex analogous to **9** (pathway ⓑ). The balance between these two channels is attained only for the dipropyl-peroxide radical cations $\mathbf{2}^{+\cdot}$–$\mathbf{4}^{+\cdot}$. In the following, we describe a simple model, which is capable to explain these results and relates the observed reactivity to thermochemical data.

The competition between pathways ⓐ and ⓑ depends on the relative heights of the barriers related to the rate-determining steps and the thermochemical product stabilities. Channel ⓐ is mainly influenced by the different degree of methyl substitution in the α-positions of the peroxides, and higher substitution of the carbonyl groups in the product ions is preferred on thermochemical grounds [14] [16]. Thus, pathway ⓐ should be favored in the order $\mathbf{5}^{+\cdot} > \mathbf{2}^{+\cdot} > \mathbf{1}^{+\cdot}$, which is partially reflected in the finding that products generated in this channel contribute to 79% (losses of $CH_3^{\cdot}$ and $[C_4,H_9,O]^{\cdot}$) of all fragmentations for $\mathbf{5}^{+\cdot}$, 78% for $\mathbf{2}^{+\cdot}$ (losses of $CH_3^{\cdot}$, $[C_3,H_7,O]^{\cdot}$, and $[C_4,H_9O]^{\cdot}$) and are not observed for $\mathbf{1}^{+\cdot}$. However, it has to be taken into account that the thermochemical stability of alkyl ions generated in channel ⓑ influences the competition between both channels as well in that the formation of t-$C_4H_9^+$ is favored over that of i-$C_3H_7^+$. In addition, for pathway ⓑ the protonation within the ion/dipole complexe **8** and the corresponding homologues constitutes a crucial step. The proton affinity of ethene ($PA = 162.6$ kcal/mol) [14] is very close to that of peroxy radicals ($PA \approx 158$ kcal/mol)9)), rendering the protonation step almost thermoneutral for $\mathbf{1}^{+\cdot}$. Thus, pathway ⓐ cannot effectively compete and is not observed in the experiments. In contrast, the *PA*s of alkenes increase from ethene and propene ($PA = 179.5$ kcal/mol) to isobutene ($PA = 195.9$ kcal/mol), resulting in a more and more endothermic proton transfer from the carbocation to the alkylperoxy radical $\mathbf{8} \rightarrow \mathbf{9}$. For $\mathbf{2}^{+\cdot}$, both pathways are comparable as far as the energetic constraints are concerned, such that a competition between both channels is observed. In the case of $\mathbf{5}^{+\cdot}$, the protonation step is endothermic by *ca.* 38 kcal/mol, and, therefore, cannot compete with the formation of t-$C_4H_9^+$ cations and

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9) For the protonation of $HO_2^{\cdot}$, a value of $PA = 158$ kcal/mol is calculated (see [16]).

methyl losses, which prevail the unimolecular dissociations of metastable $5^{+\cdot}$. In conclusion, the generalized mechanism as depicted for $2^{+\cdot}$ in *Scheme 3* together with the concept of two competing reaction channels is able to explain the observed experimental results on the basis of thermochemistry for all peroxide radical cations studied here.

Conclusions. – The results of this study provide a detailed insight into the unimolecular decay of symmetric dialkyl-peroxide radical cations. Two reaction channels have been identified, which include proton-bound dimers of carbonyl compounds and ion/dipole complexes as intermediates. One of the channels exhibits an unprecedented coupled proton and hydrogen-atom transfer as derived from the analysis of the MI mass spectra of isotopically labeled peroxides. The reaction pattern and its dependence on the structure of the peroxides has been related to thermochemical data.

In contrast to earlier studies [4], which suggested that, at least, part of the unimolecular decay of the peroxides involves initial O–O bond cleavage, the radical cations exhibit preferentially C–C and C–O bond fission. Cleavage of the O–O bond is observed as a secondary process in the course of the subsequent rearrangements of $[M - CH_3]^+$ ions to proton-bound dimers. This unexpected result is due to an enormous increase of the O–O bond dissociation energy (*BDE*) upon ionization. The *BDE*(O–O) of neutral dialkyl peroxides amounts to *ca.* 37 kcal/mol and does not change much upon increasing methyl substitution in the α-positions [21]. Instead, due to the unfavorable thermochemistry of *e.g.* the i-PrO$^+$ cations [22], the *BDE*(i-PrO – Oi-Pr$^{+\cdot}$) increases up to 63 kcal/mol^{10}). In marked contrast, in the radical cation the C–O bond has a much lower *BDE* (*ca.* 34 kcal/mol) as compared to the neutral species (*ca.* 59 kcal/mol)^{11}). Thus, the observed reactivity can be well understood on the basis of these thermochemical data.

The ionic product of $C_3H_7^{\cdot}$ losses from diisopropyl-peroxide radical-cations has been identified by MI/CA experiments to have the structure of a protonated carbonyl oxide. In the course of the reaction of O_3 with alkenes [8], several 1,3-dipolar cycloaddition steps have been postulated, including carbonyl oxides as intermediates. The product of propyl loss from $2^{+\cdot}$ can be regarded as a protonated analogue of the '*Criegee* intermediates', and further studies towards these interesting species are in progress.

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^{10}) *BDE*(i-PrO–Oi-Pr$^{+\cdot}$) = ΔH_f(i-PrO$^\cdot$) + ΔH_f(i-PrO$^+$) – ΔH_f(i-PrO–Oi-Pr$^{+\cdot}$) = 9.2 kcal/mol + 199.7 kcal/mol – 146.2 kcal/mol = 62.7 kcal/mol.

^{11}) Since thermochemical data were not available for the isopropylperoxy radical, the values reported here are those for isopropanol and the corresponding radical cation.

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