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A Hidden Hydrogen Transfer in the Unimolecular Reaction of 1,2-Dimethoxyethane$^{\bullet+}$

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The metastable dimethoxyethane radical cation **1** eliminates methanal to give the $CH_3O^+(H)CH_2C^{\bullet}H_2$ distonic ion **2** (m/z 60, 80%) and methanol to yield the $C_3H_6O^{\bullet+}$ (m/z 58, 20%) fragment. The first process is well-known, beginning with the transfer of a hydrogen from a methoxy group to the oxygen of the other to yield the intermediate distonic ion $^{\bullet}CH_2OCH_2CH_2O^+(H)CH_3$, **3**. It is shown, from FTICR experiments, that the m/z 58 fragment possesses the $CH_3OCHCH_2^{\bullet+}$ structure **5**. From energetic studies, it can be established that both fragmentations involve the same intermediate **3**. The existence of a hidden 1,4-H transfer from carbon to carbon in the formation of **5** is shown. The energy profile is elucidated by the behavior of metastably decomposing stable isotopically labeled 1,2-dimethoxyethane radical cation **1**.

Introduction

The unimolecular reactions of several $R_1CH_2CH_2R_2^{\bullet+}$ (R_1 or R_2 = OH, OCH_3, OC_2H_5, NH_2) radical cations have been the subject of several studies.[1−4] Their fragmentation mechanisms can be very different for the various substituents. For instance it has been shown that the first step of the fragmentation of $HOCH_2CH_2OH^{\bullet+}$ and $HOCH_2CH_2OCH_3^{\bullet+}$ is the simple cleavage of the C−C bond, leading to a complex that is a key intermediate in the reaction pathways.[1,2]

In contrast, Bouchoux et al.[3] have shown very recently that the fragmentation of $H_2NCH_2CH_2NH_2^{\bullet+}$ (eq 1), involves a direct 1,3-H transfer that is the rate determining step of the reaction.

$$H_2NCH_2CH_2NH_2^{\bullet+} \rightarrow H_2NCHCH_2NH_3^{\bullet+} \rightarrow CH_2CHNH_2^{\bullet+} + NH_3 \quad (1)$$

In a previous work,[4] it was proposed that the reactions of $HOCH_2CH_2OC_2H_5^{\bullet+}$, $H_5C_2OCH_2CH_2OC_2H_5^{\bullet+}$, and $H_3COCH_2CH_2OCH_3^{\bullet+}$ (**1**) begin with the transfer of a hydrogen from one alkoxy group to the oxygen of the other, giving an intermediate distonic ion. However, it was shown that the behavior of ion **1** differs completely from that of the other two ions.

In this work, the unimolecular reaction of **1** will be revisited by using FTICR to ascertain the structure(s) of the m/z 58 fragment and synchrotron radiation experiments to study energy aspects.

Experimental Section

Bimolecular reactions of reactant ions were carried out using a Bruker CMS-47X Fourier transform ion cyclotron resonance mass spectrometer equipped with an external electron ionization source[5] and an Infinity cell.[6] Ions generated in the external electron ionization source were transferred via the ion optics into the cell containing the neutral reactant at a pressure of 10^{-8} to 2×10^{-8} mbar. Unwanted ions were ejected by a combination of chirp and shot radio frequency (rf) pulses. The remaining ions were relaxed by collisions during at least 1 s with an unreactive buffer gas (argon) in the ICR cell at constant pressure (2×10^{-7} mbar if not otherwise stated) and then isolated again by soft rf shots only, avoiding unwanted excitation of the ions of interest. The exact isotopic composition of all ions was verified by high-resolution measurements using the same conditions as for broad band experiments, excepted for the argon pressure, which was reduced to 10^{-7} mbar to allow a better resolution.

Spectra of metastable ions (MIKE)[7] were collected by using a double focusing mass spectrometer (B/E geometry) VG-ZAB-2F equipped with a chemical ionization ion source ($p = 10^{-6}$ mbar). Collision-induced dissociations (CID)[7] were performed by using argon as the collision gas. Kinetic energy releases (KER)[7] were measured by taking into account the width of the main beam.

Appearance energy (AE) and ionization energy (IE) measurements were performed on the 1,2-dimethoxyethane radical cation, at LURE (Orsay, France), using the synchrotron radiation from the SuperACO storage ring and the SAPHIRS[8] and CERISES[9] experimental setups. While SAPHIRS, consisting of a short time-of-flight tube, allows the measurement of the fragmentation processes occurring within 20 μs after ionization, CERISES, making use of an octopolar ion trap, gives access to transit times and detection of parent and fragment ions between 10^{-3} and 10^{-4} s. Results obtained on these two setups therefore give information about metastable processes, as well as fragmentation thresholds with limited effects of kinetic shifts.

Results and Discussion

The metastable 1,2-dimethoxyethane radical cation **1** eliminates methanal to give the $CH_3O^+(H)CH_2C^{\bullet}H_2$ distonic ion **2** (m/z 60, 70%) with a small KER ($T_{0.5}$ = 18 meV) and methanol to yield the $C_3H_6O^{\bullet+}$ fragment (m/z 58, 30%) with a greater KER ($T_{0.5}$ = 88 meV). The first process is well-known.[4,10] The reaction begins with the transfer of a hydrogen from a methoxy group to the oxygen of the other to yield the intermediate distonic ion **3**. Elimination of CH_2O, by simple cleavage, gives **2** (Scheme 1).

Three pathways are a priori possible[11] to form the m/z 58

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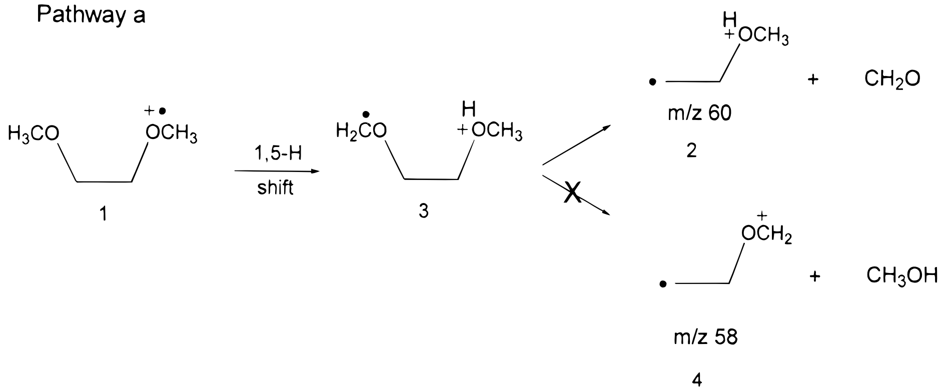

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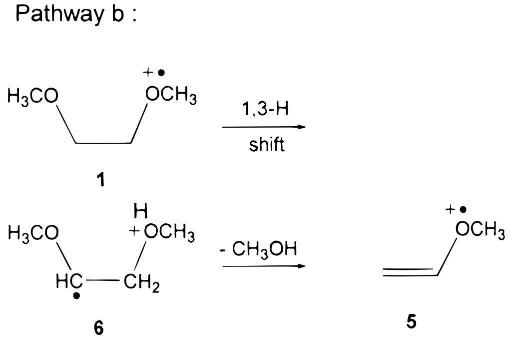

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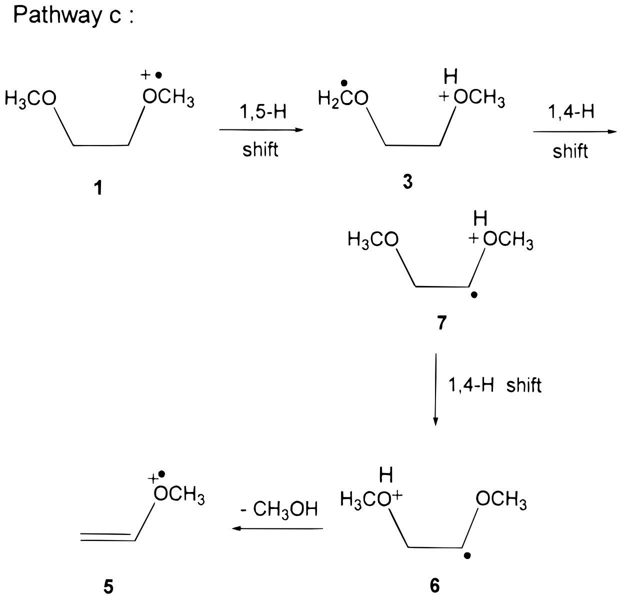

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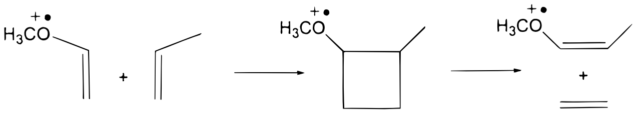


fragment. Pathway a involves a simple cleavage of **3**, leading to methanol elimination and production of the distonic ion $^{\bullet}CH_2CH_2OC^{+}H_2$ (**4**), which is an isomer of the $CH_3OCHCH_2^{\bullet+}$ radical cation **5** (Scheme 1).

Pathway b corresponds to a 1,3-H transfer from carbon to charged oxygen, giving the intermediate distonic ion **6**, which leads, by simple cleavage, to **5** and methanol loss (Scheme 2).

In pathway c, **3** is the intermediate for the *m*/*z* 58 fragment formation as well as for the *m*/*z* 60 fragment. From **3**, a 1,4-H shift from carbon to carbon gives the intermediate **7** and then **6**, by a 1,4-H transfer from oxygen to oxygen (Scheme 3). In previous work,[4] pathway c has been suggested to occur from the results of labeling, whose interpretation will be revisited further below. However, in this early work, the structure of the *m*/*z* 58 fragment was not established, while no direct proof of the intermediacy of ion **3** for both fragmentations was given.

Structure of the m/z 58 Fragment. The CID spectrum of the *m*/*z* 58 fragment formed in the ion source of a magnetic mass spectrometer and that of the same fragment formed in the first FFR, are almost identical, which means that *m*/*z* 58 corresponds to the same structure or the same mixture of structures, whatever the internal energy of the decomposing ion **1**. Furthermore, these spectra are very similar to that of methyl vinyl ether, but this method is often not sensitive enough to detect the presence of a minor other structure. In contrast, FTICR is a particularly sensitive tool for this kind of problem.[12] Some bimolecular reactions of the two a priori possible $C_3H_6O^{\bullet+}$ ions, $CH_3OCHCH_2^{\bullet+}$ (**5**) and $^{\bullet}CH_2CH_2OC^{+}H_2$ (**4**), have been described. The radical cation of methyl vinyl ether (**5**) gives rise to crossed cycloaddition/cycloreversion reactions with alkenes,[13] whereas the reactivity of distonic ion **4** is dominated by the transfer of ionized ethylene.[14,15] FTICR experiments prove that the reactions of the *m*/*z* 58 fragment, formed by the reaction shown in Scheme 3 are the same as those of the $CH_3OCHCH_2^{\bullet+}$ radical cation **5**. The ion is not reactive toward acetonitrile ($p = 6 \times 10^{-8}$ mbar, up to 30 s reaction). With methanal, cycloaddition is not observed. The *m*/*z* 58 fragment and ion **5** react with propene at the same rate by a cycloaddition/cycloreversion reaction (Scheme 4) giving methyl propenyl ether $C_4H_8O^{\bullet+}$ ($p = 4 \times 10^{-8}$ mbar, half-reaction time = 14 s). Furthermore, $H^{\bullet}$ abstraction is observed as a minor reaction pathway in both cases, with the same branching ratio. Similarly, the *m*/*z* 58 fragment and ionized methyl vinyl ether react at the same rate with C_2D_4 by cycloaddition−cycloreversion to yield ionized labeled methyl vinyl ether $C_3H_4D_2O^{\bullet+}$ ($p = 4 \times 10^{-8}$ mbar, half-reaction time = 14s).

The behavior of ion **5** contrasts with that of the $^{\bullet}CH_2CH_2$-$OC^{+}H_2$ ion (**4**), formed by fragmentation of 1,4-dioxane$^{\bullet+}$, whose reactions are completely different.[14] In the presence of acetonitrile, a rapid transfer of ionized ethylene occurs[14,15] while, with methanal, a cycloaddition process yields ionized 1,3-dioxane (*m*/*z* 88) followed by hydrogen radical loss, giving *m*/*z* 87.[16] The behavior of **5** differs also from that of the other isomers, whose formation is highly improbable in this system, such as the enol structure $CH_3C(OH)CH_2^{\bullet+}$.[12,17]

Intermediacy of 3 for Both Fragmentations. Energetic

TABLE 1: MIKE Spectra of Labeled Ions 1: Shifts of the Peaks

	m/z								
	68	65	64	63	62	61	60	59	58
$CH_3OCH_2CH_2OCH_3^{\bullet+}$ (**1**)							70.5		$\underline{29.5}$[a]
$^{13}CH_3OCH_2CH_2O^{13}CH_3^{\bullet+}$ (**1a**)						70		$\underline{30}$	
$CD_3OCD_2CD_2OCD_3^{\bullet+}$ (**1b**)	84.5		$\underline{15.5}$						
$CH_3OCD_2CD_2OCH_3^{\bullet+}$ (**1c**)			$\underline{92}$			$\underline{8}$			
$CD_3OCH_2CH_2OCD_3^{\bullet+}$ (**1d**)			52.5			$\underline{47.5}$			
$CH_3OCH_2CD_2OCD_3^{\bullet+}$ (**1e**)		58.5		19	$\underline{3}$		$\underline{19.5}$		
$CH_3OCH_2CH_2OCD_3^{\bullet+}$ (**1f**)				43.5		38[b]			$\underline{18.5}$

[a] Numbers underlined correspond to methanol loss. [b] Corresponding respectively to methanal-d_2 (21%) and methanol (17%); see ref 18.

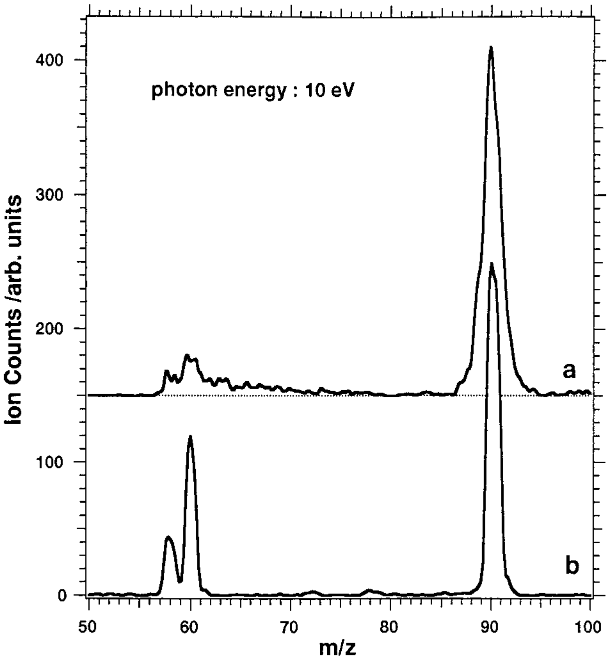


Figure 1. Ion yield curves obtained at 10 eV photon energy with two setups: (a) obtained with SAPHIRS,[8] which corresponds to detection of parent and fragments within 12 μs following ionization; (b) obtained with CERISES,[9] within 400 μs following ionization.

measurements, studied by synchrotron radiation give a clear demonstration of the existence of a common intermediate in the formation of both fragments, *m/z* 58 and *m/z* 60. Figure 1 illustrates the variability of results due to the time scale of detection. Both curves were obtained at 10 eV photon energy, but with two different setups; curve a was obtained with SAPHIRS[8] and corresponds to detection of parent and fragments within 12 μs following ionization while curve b was obtained with CERISES,[9] within 400 μs following ionization. Though curve a exhibits a much lower fragmentation yield and a metastable tail, the intensity ratio between *m/z* 58 and 60 is similar to that of curve b. These curves indicate identical time scales for the metastable processes leading to both fragments.

In Figure 2 ion yield curves are reported for the parent ion *m/z* 90 and fragments ions *m/z* 45, 58, and 60 following photoionization of 1,2-dimethoxyethane on CERISES. These curves show that the abundances of the *m/z* 58 and 60 fragments as a function of photon energy present a parallel evolution of the yield as well as an identical appearance energy:

$$\mathrm{AE}[m/z\ 58] = \mathrm{AE}[m/z\ 60] = 9.60 \pm 0.05\ \mathrm{eV}$$

These results demonstrate the likelihood of an identical rate-limiting step for both fragments. We propose this common step to be the inital 1,5-H transfer from a methoxy group to the oxygen of the other in the molecular ion of 1,2-dimethoxyethane, leading to the distonic ion **3**.

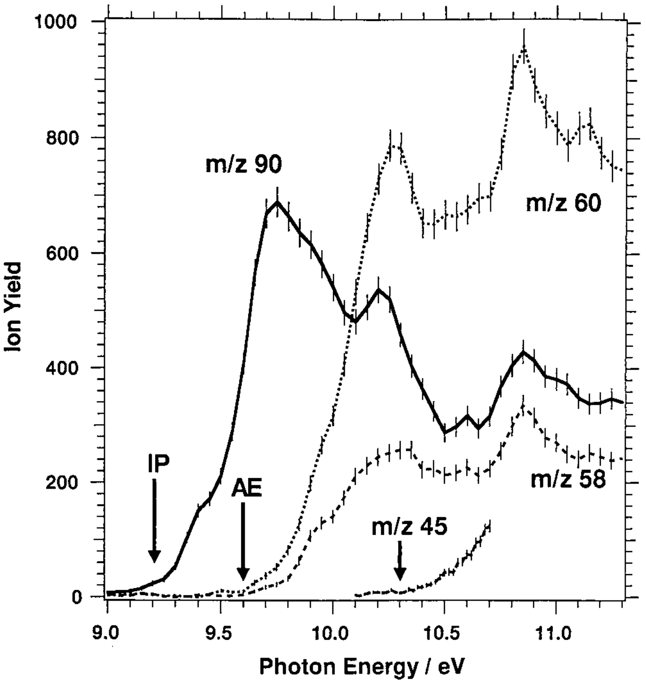


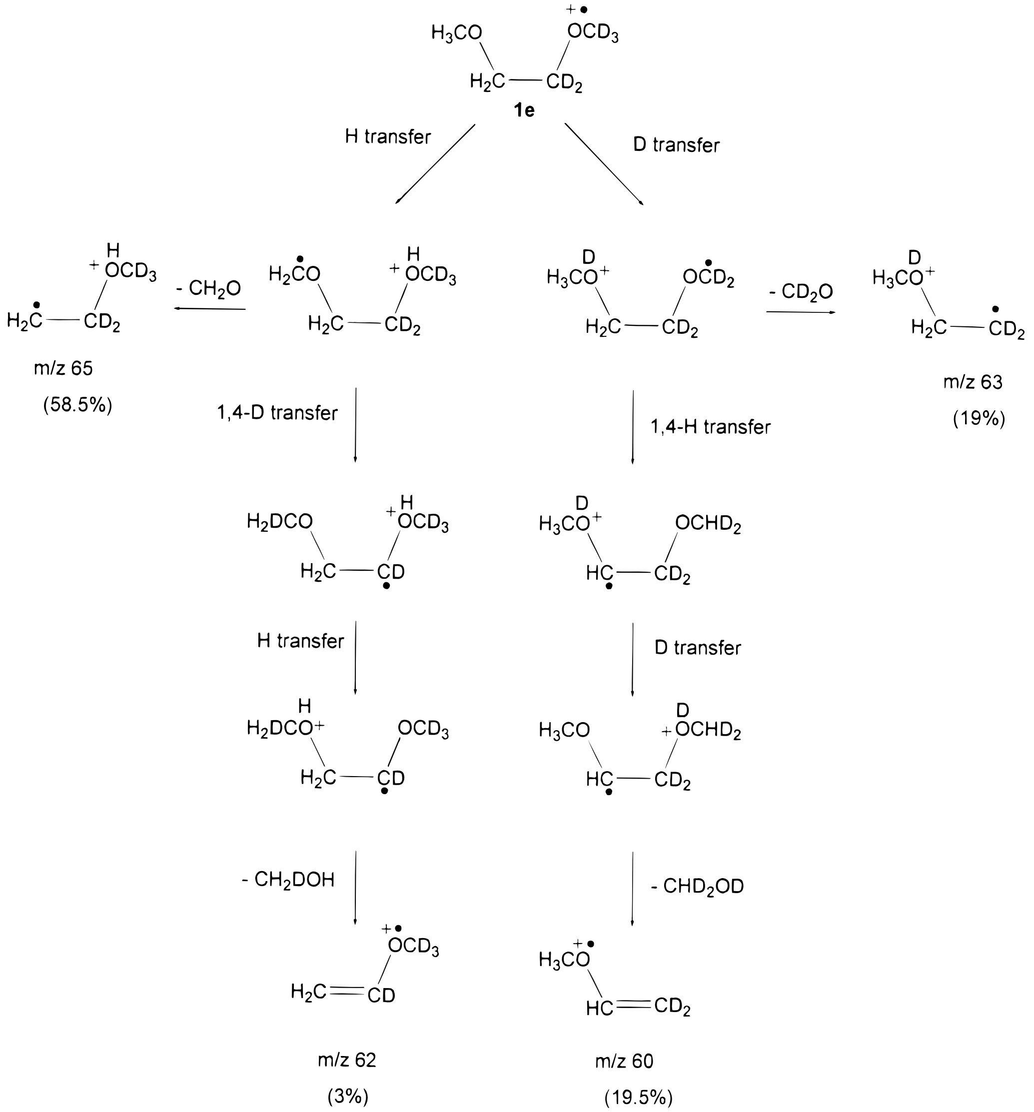
Figure 2. Ion yield curves for the parent and *m/z* 45, 58, and 60 from 1,2-dimethoxyethane obtained on CERISES.[9]

Labeling Revisited. The structure of the final ions and the intermediacy of **3** in both fragmentations having been established, the interpretation of the behavior of labeled ions **1**[4] will be reexamined.[18] On one hand, the shift of the peaks in the MIKE spectra reported in Table 1 are in agreement with the pathway c, while the ^{13}C-labeled ion **1a** confirms that there is no carbon permutation prior to dissociation. On the other hand, the relative abundances of the fragments reflect several primary and secondary isotope effects.[19]

The metastable $CH_3OCD_2CD_2OCH_3^{\bullet+}$ ion (**1c**) yields the pure isotopomer fragments *m/z* 61 ($C_3D_3H_3O^{\bullet+}$, loss of CH_3OD, 8%) and *m/z* 64 ($C_3D_4H_4O^{\bullet+}$, loss of CH_2O, 92%). This shows first that a methoxy group and one hydrogen of a methylene group are involved in the methanol molecule that is eliminated, which confirms the structure **5** for the final ion (Scheme 2). The branching ratio between methanal loss and methanol loss is about 11.5 in **1c** and only 2.4 for the unlabeled ion **1**. The significant isotope effect indicates that the 1,4-H transfer of a methylene hydrogen to the radical carbon involves a significant energy barrier, even if its transition state is lower than that corresponding to the first H transfer. In agreement with this conclusion, the 1,4-H transfer is irreversible since no H exchange precedes the dissociation.

Two kinds of isotope effects, which are difficult to separate, are concerned in the first H transfer. The influence of the primary one is indicated by comparing the total abundance of both fragments coming either from an initial H transfer or from

SCHEME 5



an initial D transfer (**1e** and **1f**). In contrast, the secondary one can be shown by comparing the branching ratio between methanal and methanol for a same first step, which can be either a H transfer or D transfer.

In the metastable $CH_3OCH_2CD_2OCD_3^{\bullet+}$ ion (**1e**) (Scheme 5), the initial H transfer leads to *m*/*z* 62 (CH_2DOH loss, 3%) and *m*/*z* 65 (CH_2O loss, 58.5%) according to Scheme 3. The initial D transfer leads to *m*/*z* 60 (CHD_2OD loss, 19.5%) and *m*/*z* 63 (CD_2O loss, 19%). The data indicate that the first step of the reaction (**1** → **3**) is accompanied by an isotope effect since the fragments coming respectively from the initial H and the D transfer are in a branching ratio of 61.5:38.5 (1.6). The low abundance of the *m*/*z* 62 fragment also confirms that, starting now from the intermediate **3**, its simple cleavage giving the fragment **2** is in competition with the 1,4-D shift leading to **7** (and then **5**). Similarly, in the metastable $CH_3OCH_2CH_2OCD_3^{\bullet+}$ ion (**1f**), a comparable ratio is found.

The competition between (**3** → **2**) by simple cleavage and (**3** → **7** → **5**) also involves a secondary isotope effect when the formation of ion **2** occurs with CD_2O loss, as is exemplified by the differences in the MIKE spectra between the ions possessing two OCH_3 groups (**1** and **1c**) and the corresponding ions possessing two OCD_3 groups (respectively **1d** and **1b**). The methanal and methanol losses are in a 2.4 ratio in **1** and only 1.1 (*m*/*z* 64:*m*/*z* 61) in **1d** for the ions with unlabeled methylene groups. For the ions with two labeled methylene groups, the ratio is 11.5 in **1c** and only 5.5 in **1b**. Coming back to **1e**, it can be noted that the *m*/*z* 63 (methanal loss) and *m*/*z* 60 (methanol loss) fragments, resulting both from an initial D transfer have the same abundance, in good agreement with 1.1 ratio measured in **1d**.

In conclusion, if it is assumed that there is a negligible isotope effect in the final H (D) transfer from oxygen to oxygen, then the accumulated isotope effect data can be summarized in the following way:

(i) H vs D transfer from methoxy methyl to the opposite methoxy oxygen is favored by roughly 3:2.

(ii) After this initial transfer, when subsequent 1,4-H transfer competes with CD_2O elimination, there is nearly a 1:1 probability for the two events. However, when a 1,4-D transfer competes with CH_2O elimination (see Scheme 5), there is a 95:5 probability in favor of CH_2O elimination.

(iii) The data of (i) and (ii) combined for the unlabeled and fully labeled ions **1** show that there is a pronounced isotope effect favoring 1,4-H transfer over 1,4-D transfer but CH_2O elimination is also dramatically favored over CD_2O elimination. In several of the cases shown, these effects are opposite to the complex behavior shown.

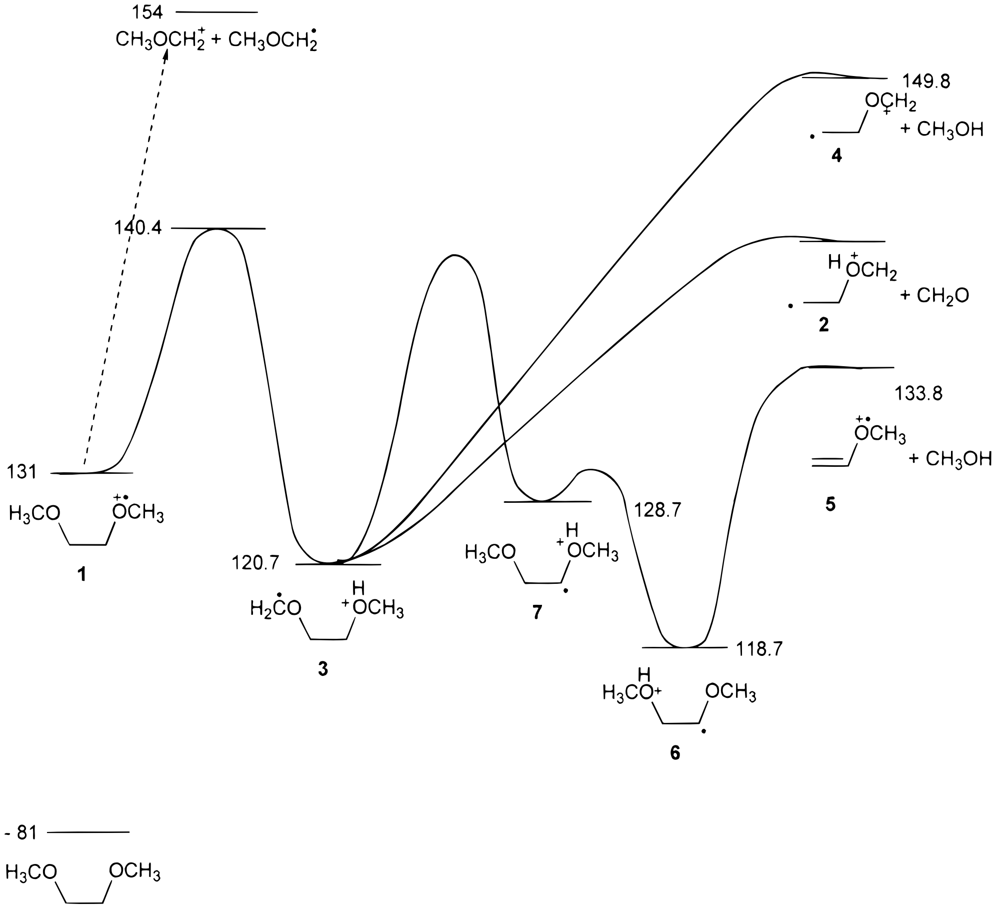


Figure 3. Energy profile (not to scale) of the unimolecular reaction of ion **1** (ΔH_f in kcal/mol).

All the data support energy requirements that are very close for the two channels.

Energy Profile. IE and AE measurements performed on the 1,2-dimethoxyethane radical cation give IE[1,2-dimethoxyethane] = 9.2 ± 0.05 eV (212 ±1.2 kcal/mol) and AE[*m/z* 58] = 9.6 ± 0.05 eV (221.4 ± 1.2 kcal/mol). Therefore, using ΔH_f[1,2-dimethoxyethane] = −81 kcal/mol,[20] we find (i) ΔH_f[1,2-dimethoxyethane$^{•+}$] = 131 kcal/mol (in good agreement with ref 20) and (ii) 140.4 kcal/mol for the energy of the transition state leading to *m/z* 58 formation. Using $\Delta H_f[CH_3OH] = -48.2$ kcal/mol,[20] the maximum value of the ΔH_f[*m/z* 58] is 188.6 kcal/mol. This value rules out the structure $^•CH_2CH_2OC^+H_2$ (**4**) (ΔH_f = 198 kcal/mol[15]) but is in agreement with the formation of $CH_3OCHCH_2^{•+}$ (**5**) (ΔH_f = 182 kcal/mol[20]).

To visualize the reaction pathway, the energy profile proposed in Figure 3 was elaborated from an evaluation of the enthalpy of the intermediate distonic ions by the usual approximation method.[10] ΔH_f[**3**] = 120.7 kcal/mol was obtained from $\Delta H_f[CH_3OCH_2^•] = -3$ kcal/mol,[16] $\Delta H_f[CH_3OCH_3] = -44$ kcal/mol,[20] and the proton affinity of 1,2-dimethoxyethane PA = 205 kcal/mol.[21] ΔH_f[**6**] = 118.7 kcal/mol was considered to differ from ΔH_f[**3**] by the difference in the bond strength of a primary and a secondary C−H bond (about 2 kcal/mol[20]). The proximity between the charge and the radical in the α-distonic ion **7** introduces a destabilization of the ion that has been determined to be 10 kcal/mol[22] for the α-distonic ion $CH_3O^+(H)C^•H_2$ compared with protonated dimethyl ether. This leads to the indicative value ΔH_f[**7**] = 128.7 kcal/mol.

The energy profile indicates that the initial 1,5-H transfer (**1** → **3**), from carbon to oxygen, requires 9.4 kcal, which is rather low if it is taken into account that a primary hydrogen is transferred. The last 1,4-H shift from oxygen to oxygen (**7** → **6**) is known to be facile and may be almost barrier free.[23] In contrast, 1,4-H transfers from carbon to carbon are known to be difficult. To give an order of magnitude, the isomerization of the system shown in eq 2, which is rather similar to that studied in this work, has been calculated to require 20.8 kcal/mol.[24,25]

$$CH_3CH_2O^+(H)C^•HCH_3 \rightarrow {}^•CH_2CH_2O^+(H)CH_2CH_3 \quad (2)$$

This high barrier can be overcome when **1** fragments via pathway c, only because the intermediate distonic ions lie very low in energy compared with **1**. From the enthalpy of formation and from the results of refs 24 and 25, it can be considered that the transition state for the 1,4-H transfer (**3** → **7**) is likely to be very close to the transition state for the first transfer (**1** → **3**).

The energy profile is in good agreement with the significant isotope effect observed for both transfers. It also shows that the reverse activation energy in the formation of **5** is about 6.5 kcal/mol (from our AE results) which is consistent with the non-negligible kinetic energy release (88 meV), which is measured. In contrast, the small kinetic energy (18 meV) obtained for the formation of **2** suggests that the corresponding final state must lie near the threshold. The determination of ΔH_f[**2**] will be discussed elsewere; the value proposed by McAdoo[25] leads to a final state situated 4 kcal under the AE measured in this work, while that determined by Holmes[26] lies 4 kcal above, from AE measurement also.

Finally, it must be noted that the simple cleavage of **1** leads to the $CH_3OCH_2^+$ fragment (*m/z* 45) whose measured EA (10.3 eV) is in agreement with $\Delta H_f[CH_3OCH_2^+] = 157$ kcal/mol[20] and $\Delta H_f[CH_3OCH_2^{\bullet}] = -3$ kcal/mol.[20] The corresponding final state lies in energy far above the measured transition states giving *m*/*z* 58 and 60. The *m*/*z* 45 fragment is not observed when the low-energy ions **1** decompose but is favored when the internal energy increases or upon collision. The CID spectra of **1e** shows *m*/*z* 45 and 50 fragments in a 51.5:48.5 ratio, while in **1f**, *m*/*z* 45 and 48 are in a 52.5/47.5 ratio. This shows that the dominant fragmentation in the ion source (the simple cleavage of **1**) occurs almost without a secondary isotope effect and has therefore no influence on the internal energy distribution of ions **1** in the second FFR.

Comparisons. The mechanism proposed for ionized 1,2-dimethoxyethane (pathway c, Scheme 2) contrasts with that demonstrated by Bouchoux et al.[3] for the fragmentation of $H_2NCH_2CH_2NH_2^{\bullet+}$ (eq 1). The unimolecular reaction of this radical cation, whose chain is shorter, involves a direct 1,3-H transfer that would correspond to the pathway b. In this case the 1,3-H transfer is the rate-determining step of the reaction. The energy barrier has been calculated to be about 20 kcal/mol[3].

This calculated value for a 1,3-H shift is less than that calculated for ionized ethylamine (32 kcal/mol[27]), for which a primary hydrogen is transferred. In comparison, the values calculated for a 1,2-H transfer from carbon to heteroatoms (35 kcal/mol in ionized dimethyl ether[28] and 39 kcal/mol for ionized methylamine[27]) are slightly higher. In contrast, 1,4-H transfers (13.5 kcal/mol[27]) and 1,5-H transfers are more facile. These calculations confirm experimental data. In *n*-alkyl alcohols,[29] *n*-alkyl ethers,[30] or *n*-alkylamine[31] radical cations, the fragmentation begins by a long distance H transfer to the heteroatom (including 1,4- or 1,5-H shifts), but never by a 1,2- or a 1,3-H transfer. Conversely, α- and *β*-distonic ions $^{\bullet}CH_2XH^+$ and $^{\bullet}CH_2CH_2XH^+$ ($X = OH$, OCH_3, NH_2, etc.) are known to be stable species since their isomerization into their molecular ion counterparts necessitates high energy barriers.[10]

In the case studied, the high energy barrier that may be involved in a 1,3-H shift (**1** → **6**) makes the pathway b more energy demanding than the pathway c involving three successive H shifts, which is indeed the only one to occur.

Conclusion

The metastable dimethoxyethane radical cation **1** eliminates methanal to give the $CH_3O^+(H)CH_2C^{\bullet}H_2$ distonic ion **2** (*m*/*z* 60, 70%) and methanol to yield the $CH_3OCHCH_2^{\bullet+}$ fragment **5** (*m*/*z* 58, 30%).

The behavior of **1** contrasts with that of $H_2NCH_2CH_2NH_2^{\bullet+}$, which involves a direct 1,3-H transfer from a methylene group to the heteroatom.[3] In the case of **1**, the reaction begins by the transfer of a hydrogen from a methoxy group to the oxygen of the other to yield the same intermediate distonic ion **3** for both fragmentations. Ion **3** either undergoes a simple cleavage giving **2** or a 1,4-H shift from carbon to carbon leading to the intermediate distonic ion **7**, followed by a 1,4-H shift from oxygen to oxygen giving **6**, whose simple cleavage yields **5** and loss of methanol.

The global result of the reactions of ion **1** and of $H_2NCH_2CH_2NH_2^{\bullet+}$ is *in appearance* identical: formation of a fragment possessing a vinyl structure with retention of one methylene hydrogen in the neutral moiety eliminated. However, in **1**, the length of the chain allows a hidden triple H transfer that is less energy demanding than a direct 1,3-H shift. Similar mechanisms involving a hidden H transfer have been proposed in early works to explain the unimolecular reactions of ionized heptylamine[31] or that of ionized alkanoic acids.[32]

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(19) It may be also possible that the nature (H or D) of the first transfer changes the energy content of the intermediate **3**. In contrast, it will be shown further below, that the simple cleavage giving *m*/*z* 45, dominant in the ion source, occurs without isotope effect and has, therefore, no influence on the internal energy distribution in the ion source.

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