Mechanisms and Stereochemistry of Acid-Induced Ring Opening of Optically Active 1,2-Propene Oxides in the Gas Phase**

Anna Troiani, Antonello Filippi, and Maurizio Speranza*

Abstract: The acid-induced ring opening of (*S*)-(−)-1,2-propene oxide (**1S**) and (*R*)-(+)-1,2-propene oxide (**1R**) has been investigated in gaseous CH_4 and CH_3F at 720 torr and in the presence of a nucleophile, NuOH (Nu = H or CH_3). The mechanism of the ring-opening reaction has been assessed by modulating the composition of the gaseous mixture. Two reaction pathways are operative in the gas phase, both proceeding through complete inversion of configuration of the reaction center. A first process is detectable only in the CH_3F/H_2O systems and takes place within a persistent proton-bound complex generated by interaction of the epoxide with the $CH_3OH_2^+$ ion, formed by methylation of H_2O with $(CH_3)_2F^+$. Such an *intracomplex* ring-opening pathway proceeds through proton transfer from the $CH_3OH_2^+$ ion to the epoxide followed by motion of the neutral CH_3OH moiety around the 1-H-oxonia-2-methyl-cyclopropane structure (H-**1R** or H-**1S**) ($k < 10^8\ s^{-1}$) before attacking the ring carbons from the rear. In all the other systems with added CH_3OH, this *intracomplex* pathway is preceded by a faster "*extracomplex*" pathway involving the attack of an external CH_3OH molecule on the proton-bound adduct. The regioselectivity of the *intracomplex* process is similar to that of the *extracomplex* pathway. Both are characterized by a slight preference for the C_β center of H-**1R** (or H-**1S**) (*extracomplex* path regioselectivity: $\alpha/\beta = 0.72 \pm 0.05$; *intracomplex* path regioselectivity: $\alpha/\beta = 0.71 \pm 0.05$). The regioselectivity of H-**1R** (or H-**1S**) is substantially different from that of the 1-Me-oxonia-2-methyl-cyclopropanes (Me-**1R** or Me-**1S**) toward the same nucleophile NuOH ($\alpha/\beta = 4.13 \pm 0.35$ (Nu = H); 2.28 ± 0.16 (Nu = CH_3)). This difference is attributed to a transition structure wherein the C_α–O bond rupture increases from H-**1R** (or H-**1S**) to Me-**1R** (or Me-**1S**) and in passing from CH_3OH to H_2O. The regio- and stereoselectivity of the gas-phase acid-induced ring opening of **1S** and **1R** are compared with those of related reactions carried out in solution.

Keywords
chirality · gas-phase chemistry · ion–molecule reactions · regioselectivity · ring-opening reactions

Introduction

The mechanism and the stereochemistry of acid-catalyzed ring opening of 1,2-epoxides in solution depend to a large extent on several intrinsic factors, such as the structure of the epoxide, the nature of substituent groups, and their location relative to the epoxy ring, as well as on environmental factors, including the polarity and the nucleophilicity of the solvent, the nature of the acid catalyst, the temperature, and so on.[2] Thus, for instance, acid-catalyzed alcoholysis of epoxides was found to proceed by all the possible mechanisms, from the A1 to the A2 extremes (Scheme 1),[3] with a stereochemistry ranging from complete retention to complete inversion of configuration.[4] Acid-catalyzed ring opening of the simplest unsymmetrically substituted epoxide, that is, 1,2-propene oxide, proceeds through various mechanisms depending on the specific reaction site, that is, an A2 reaction at the unsubstituted and a borderline A1–A2 reaction at the methyl-substituted carbon.[3, 5] The relative importance of these processes is determined by the ionic or neutral character of the epoxy substrate as well as by the nucleophilicity of the reaction medium. Accordingly, the regioselectivity of ring opening of 1,2-propene oxide in water responds to the pH and the ionic strength of the reaction medium. Thus, predominant substitution at the unsubstituted carbon was observed at pH 7 in the presence of salts, whereas prevailing substitution at the methyl-substituted carbon was observed at pH 1.[5] No information about possible concomitant variations in the stereochemistry of the process was provided in these studies.

In view of these considerations, discrimination between the intrinsic and the environmental factors governing the mechanism and the stereochemistry of acid-induced ring opening in 1,2-propene oxide would be possible only by eliminating the reaction medium, namely by carrying out the reaction in the isolated state, where the nature of the active intermediates can be better defined and their evolution to products is unaffected by solvation and ion-pairing phenomena. However, to stand

[*] Prof. M. Speranza, Dr. A. Troiani, Dr. A. Filippi
Facoltà di Farmacia, Dipartimento di Studi di Chimica e Tecnologia delle Sostanze Biologicamente Attive
Università degli Studi di Roma "La Sapienza"
P.le A. Moro 5, 00185 Rome (Italy)
Fax: Int. code +(6)4991-3602
e-mail: speranza@axrma.uniroma1.it

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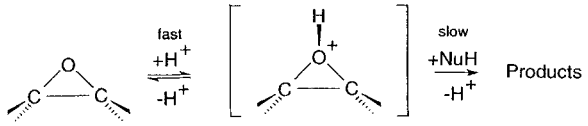
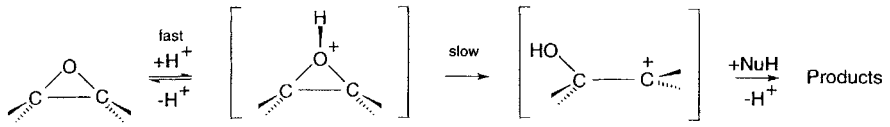
– The bimolecular addition (A2) mechanism:



– The unimolecular addition (A1) mechanism:



Scheme 1. Acid-catalyzed alcoholysis of by A1 and A2 mechanisms.

comparison with the corresponding processes in solution, the reaction carried out under these ideal conditions must still obey thermal kinetics, which means that the reaction intermediates must be in constant thermal equilibrium with the missing reaction medium. A reasonable compromise to settle this evident contradiction, at least in part, is to carry out the reaction in an inert bulk gas, at a pressure ensuring efficient thermal equilibration of the reaction intermediates by multiple unreactive collisions with the gaseous medium, wherein the concentration of the active species is kept low enough to avoid formation of organized clusters around the ionic intermediates prior to their evolution to products.

The present study is aimed at investigating the mechanism and the stereochemistry of acid-induced ring opening in 1,2-propene oxide under typical gas-phase nucleophilic conditions. For these purposes, stationary concentrations of gaseous Brønsted, that is, $C_nH_5^+$ ($n = 1$, 2), and Lewis acids, that is, $(CH_3)_2F^+$, have been generated from γ-radiolysis of their neutral precursors, that is, CH_4 and CH_3F (720 torr), respectively, in the presence of traces of the chiral epoxide, either (*S*)-(−)-1,2-propene oxide (**1S**) or (*R*)-(+)-1,2-propene oxide (**1R**) (ca. 4 torr) and of a nucleophile, NuOH (Nu = H or CH_3) (ca. 3 torr). Under such conditions, the gaseous acids efficiently attack all the bases present in the gaseous mixture, including the epoxy substrate, to yield the corresponding conjugate species. These ionic species may aggregate with several molecules of the bulk gas at the pressure and temperature employed. However, when these clusters interact with the first NuOH molecule, extensive declustering of the ionic intermediate may take place as a means of dissipating most of the energy developed in the clustered ion–NuOH interaction. Full thermalization of the ensuing encounter complex is completed by fast multiple collisions with the bulk gas (10^{10} s^{-1}) prior to its conversion to reaction products. The regio- and stereochemistry of the ring-opening reaction occurring in these thermalized encounter complexes may be inferred from the yield and the composition of the neutral substituted products.

It is hoped that this study, which represents the first stereochemical investigation on chiral epoxides in the gaseous phase, may provide some insight into the properties of these ion–neutral encounters and on the mechanism and the stereochemistry of their evolution to the epoxy ring opening products. Furthermore, a comparison of the gas-phase results with the relevant solvolytic data may contribute to evaluate the role of environmental factors in affecting acid-induced hydrolysis and alcoholysis of epoxides in solution. An understanding of the intrinsic structural and electronic factors governing this model reaction, besides being of general interest in basic chemical research, may shed some light on the biogenesis of carcinogenic and mutagenic agents from the 1,2-epoxy metabolites of polycyclic aromatic hydrocarbons.[6]

Results

Table 1 lists the major products obtained from γ-irradiation at room temperature of gaseous mixtures containing **1S** (or **1R**) as substrate, CH_4 (or CH_3F) as the bulk gas (720 torr), O_2 (4 torr), as a thermal radical scavenger, and a nucleophile NuOH (Nu = H or CH_3; ca. 3 torr). The figures in Table 1 represent the mean distribution of the products (*S*)- (**2S**) and (*R*)-2-methoxy-1-propanol (**2R**), (*S*)- (**3S**) and (*R*)-1-methoxy-2-propanol (**3R**), and (*S*)- (**4S**) and (*R*)-1,2-dimethoxypropane (**4R**), as obtained from several GC–FID analyses of the reaction mixtures, the reproducibility of which is expressed by the

Table 1. Product yields from the gas-phase attack of $C_nH_5^+$ ($n = 1$, 2) and $(CH_3)_2F^+$ ions on **1S** and **1R** in the presence of several nucleophiles.

System composition, torr [a]			Relative product yields, % [b]						Total absolute yield
Bulk gas	Substrate	NuOH	**2S**	**2R**	**3S**	**3R**	**4S**	**4R**	G(*M*) [c]
CH_4	**1S**, 4.1	MeOH, 3.1	–	48	52	–			0.64
CH_4	**1R**, 4.1	MeOH, 2.8	44	–	–	56			0.71
CH_3F	**1S**, 4.0	H_2**O**, 3.2	9(7)	26(26)	35(33)	30(34)			0.07
CH_3F	**1R**, 4.0	H_2**O**, 3.0	23(24)	9(8)	32(32)	36(36)			0.05
CH_3F	**1S**, 4.0	Me**O**H, 3.4	–(–)	35(36)	46(47)	2(–)	5(5)	12(12)	0.80
CH_3F	**1R**, 4.7	Me**O**H, 3.1	34(35)	1(–)	2(–)	50(52)	9(9)	4(4)	1.06
CH_3F	**1S**, 4.6	**Me**OH, 3.0	1(–)	33(34)	48(50)	3(–)	5(5)	10(11)	1.26
CH_3F	**1R**, 4.7	**Me**OH, 2.8	32(34)	1(–)	5(–)	43(45)	13(14)	6(7)	0.97

[a] Bulk gas: 720 torr; O_2:4 torr. Radiation dose 2×10^4 Gy (dose rate: 1×10^4 Gy h^{-1}). The **O** and **Me** notations in the nucleophile refer to the ^{18}O and CD_3 markers, respectively. [b] Derived from GC analyses with FID detection and expressed as the percent ratio between the yield of any given product and the overall yield of the corresponding glycol derivatives. The figures in parentheses refer to relative yields of the labeled products measured by GC-MS (see text). [c] Absolute yields, expressed as the G(M) values of products, that is, the number of molecules M produced per 100 eV of energy absorbed by the gaseous mixture. Each value is the average of several determinations, with an uncertainty level of ca. 5%.

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uncertainty level quoted. The absolute yields, expressed as the number of molecules M produced per 100 eV of energy absorbed by the gaseous mixture (G(M) values), were measured at a total dose of 2×10^4 Gy (dose rate: 3×10^3 Gy h^{-1}) and found to depend critically upon the composition of the reaction mixture. Indeed, significant G(M) values (ca. 0.6–1.3) were measured in the systems with NuOH = methanol, while the same values dropped by a factor from ca. 9 to over 25 in the corresponding mixtures with NuOH = water. Addition to the gaseous mixtures of 3 torr of a strong base, such as $N(CH_3)_3$ (proton affinity (PA) = 225.1 kcal mol^{-1}),[7] causes a pronounced decrease (>80%) in the overall G(M) value of products.

The GC-FID product patterns from the irradiated CH_4/methanol mixtures are characterized by the formation of equal amounts of the 2-methoxy-1-propanol (**2**) with a configuration *inverted* with respect to that of the starting epoxide (44–48%) and of the 1-methoxy-2-propanol (**3**) with a configuration *retained* with respect to that of the starting epoxide (52–56%) (Table 1). The GC-FID product patterns from the CH_3F/methanol systems are characterized by the predominant formation of isomeric methoxypropanols **2** and **3** (81–87%), accompanied by minor amounts of the expected dimethoxypropane **4** (13–19%). The *inverted* 2-methoxy-1-propanol (**2**) [*inverted*-**2**]/{[*inverted*-**2**] + [*retained*-**2**]} > 0.97) and the *retained* 1-methoxy-2-propanol (**3**) ([*retained*-**3**]/{[*inverted*-**3**] + [*retained*-**3**]} > 0.90) are predominantly formed. A mixture of both *inverted* and *retained* dimethoxypropane **4** is also formed, with the *inverted* enantiomer slightly prevailing (67–71%). The product patterns from the $CH_3F/H_2{}^{18}O$ mixtures are characterized by the predominant formation of the quasi-racemic mixture of **3**, together with minor amounts of isomeric methoxypropanol **2** (32–35%), with the *inverted* enantiomer prevailing over the *retained* one ([*inverted*-**2**]/{[*inverted*-**2**] + [*retained*-**2**]} > 0.70).

The presence and the specific position of the isotopic label in the products **2**–**4** from NuOH containing various isotopic markers, that is, either ^{18}O or CD_3 (denoted as **O** and **Me**, respectively, in Table 1), are readily determined by their GC–MS spectra, characterized by the predominant C1–C2 bond cleavage in the corresponding molecular ions. Accordingly, **2** displays two prominent peaks at $m/z = 59$ ($[CH_3C(H)OCH_3]^+$) and $m/z = 31$ ($[CH_2OH]^+$) with an intensity ratio of ca. 9:4. Compound **3** exhibits a major peak at $m/z = 45$, due to the isobaric $[CH_3C(H)OH]^+$ and $[CH_2OCH_3]^+$ fragments, and a minor signal at $m/z = 47$ amounting to ca. 25% of the peak at $m/z = 45$ and attributed to $[CH_3O(H)CH_3]^+$. This assignment is supported by the mass spectrum of labeled **3**, $CH_3CH(OH)CH_2{}^{18}OCH_3$, which gives the fragments $m/z = 45$ ($[CH_3C(H)OH]^+$) and 47 ($[CH_2{}^{18}OCH_3]^+$) in a ratio of ca. 9:4, accompanied by a minor peak at $m/z = 49$ ($[CH_3{}^{18}O(H)CH_3]^+$) of ca. 25% of the combined intensity of the $m/z = 45$ and $m/z = 47$ signals. 1,2-Dimethoxypropane (**4**) shows two intense peaks at $m/z = 59$ ($[CH_3C(H)OCH_3]^+$) and 45 ($[CH_2OCH_3]^+$) in a proportion of approximately 13:3.

With due alteration of details in comparing cases, the same fragmentation patterns are anticipated for the labeled products **2**–**4** (Table 2). Thus, detection of the appropriate $m/z = 49$ signal ($[CH_3{}^{18}O(H)CH_3]^+$) in the mass spectrum of ^{18}O-labeled *retained* **3**, together with the major $m/z = 45$ ($[CH_3C(H)OH]^+$ and $[CH_2OCH_3]^+$) and $m/z = 47$ ($[CH_2{}^{18}OCH_3]^+$) peaks, is indicative of the exclusive presence of the isotopic marker at the methoxy group of the product. The complete absence of the same signal in the mass spectrum of ^{18}O-labeled *inverted* **3**, coupled with a higher intensity of the $m/z = 47$ ($[CH_3C(H)^{18}OH]^+$), relative to that of $m/z = 45$ ($[CH_3C(H)OH]^+$ and $[CH_2OCH_3]^+$), suggests predominant ^{18}O-incorporation in the hydroxy group of the compound. A similar pattern is observed in the mass spectrum of *retained* $CH_3CH(OH)CH_2OCD_3$, where peaks at $m/z = 50$ ($[CH_3O(H)CD_3]^+$) and $m/z = 48$ ($[CH_2OCD_3]^+$) are observed instead of the corresponding $m/z = 49$ and $m/z = 47$ signals. In the mass spectrum of *retained* **2**, detection of a signal with $m/z = 33$ ($[CH_2{}^{18}OH]^+$) denotes incorporation of the ^{18}O label in its hydroxy group, whereas the presence of a peak at $m/z = 61$ ($[CH_3C(H)^{18}OCH_3]^+$) among those of *inverted* **2** and **4** indicates ^{18}O-labeling at the C2 methoxy group. Of course, the $m/z = 61$ signal is replaced in *retained* $CH_3CH(OCD_3)CH_2OH$ by that at $m/z = 62$ ($[CH_3C(H)OCD_3]^+$). Finally, the presence of the ^{18}O label at the C1-methoxy group of *retained* **4** is signaled by the observation of an $m/z = 47$ peak ($[CH_2{}^{18}OCH_3]^+$), which is replaced by the corresponding $m/z = 48$ ($[CH_2OCD_3]^+$) signal in the mass spectrum of the $CH_3CH(OCH_3)CH_2OCD_3$ analogue. All these major fragments are indeed detected in the mass spectra of the relevant products and their abundance relative to the $m/z = 45$ fragment of the *retained* 1-methoxy-2-propanol product reported in Table 2. No significant isotope effect on the C1–C2 bond fragmentation in **2**–**4** is observed, as shown by the similar propor-

Table 2. Major ionic fragments in the mass spectra of products from the gas-phase attack of $(CH_3)_2F^+$ ions on **1S** and **1R** in the presence of several labeled nucleophiles.

System [a]	Radiolytic products (m/z) [b]					
	2S	**2R**	**3S**	**3R**	**4S**	**4R**
CH_3F/**1S**/H_2O	0.17(59)	0.15(61)	0.07(49)	0.42(47)		
	0.04(33)	0.43(59)	0.28(47)	0.74(45)		
	0.15(31)	0.42(31)	1.00(45)			
CH_3F/**1R**/H_2O	0.12(61)	0.19(59)	0.38(47)	0.06(49)		
	0.40(59)	0.03(33)	0.79(45)	0.28(47)		
	0.33(31)	0.12(31)		1.00(45)		
CH_3F/**1S**/MeOH	0.01(59)	0.81(61)	0.30(49)	0.02(47)	0.15(59)	0.31(61)
	0.01(31)	0.09(59)	0.42(47)	0.05(45)	0.03(47)	0.04(59)
		0.42(31)	1.00(45)		0.01(45)	0.08(45)
CH_3F/**1R**/MeOH	0.72(61)	0.01(59)	0.01(47)	0.31(49)	0.21(61)	0.10(59)
	0.07(59)	0.02(31)	0.07(45)	0.41(47)	0.02(59)	0.02(47)
	0.38(31)			1.00(45)	0.06(45)	0.01(45)
CH_3F/**1S**/**Me**OH	0.02(59)	0.93(62)	0.36(50)	0.03(47)	0.13(59)	0.30(62)
	0.01(31)	0.07(59)	0.43(48)	0.11(45)	0.02(48)	0.02(59)
		0.22(31)	0.01(47)		0.02(45)	0.05(45)
			1.00(45)			
CH_3F/**1R**/**Me**OH	0.99(62)	0.02(59)	0.04(47)	0.35(50)	0.44(62)	0.21(59)
	0.08(59)	0.03(31)	0.16(45)	0.43(48)	0.03(59)	0.04(48)
	0.25(31)			0.01(47)	0.08(45)	0.01(45)
				1.00(45)		

[a] Bulk CH_3F gas: 720 torr. The bold **O** and **Me** notations in the nucleophile refer to the ^{18}O and CD_3 markers, respectively. [b] Expressed as the intensity of the peak of any given fragment (m/z value given in parentheses) relative to that of the peak at $m/z = 45$ for *retained* **3** (see text). Each value is the average of several determinations, with an uncertainty level of ca. 5% and a detection limit below 0.5% for $m/z = 45$. Electron impact on unlabeled 1-methoxy-2-propanols **3** produces both the [$m/z = 45$] and the [$m/z = 47$] fragments in a 4:1 ratio.

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tions of the ionic fragments from the systems with MeOH and MeOH.

The mean relative distributions of the *labeled* products from systems containing labeled NuOH, as calculated according to the procedure illustrated in the Appendix, are reported in parentheses in Table 1. Their analysis is particularly telling as regards the nature and the stereochemistry of the reactions involved in their formation. Thus, in all CH_3F/labeled methanol systems, the isotopic signature is found exclusively in the methoxy groups of the *inverted* **2** and of the *retained* **3**, and in those bound to the C2 position of *inverted* **4** and to the C1 atom of *retained* **4** (Table 2). When generated from irradiation of mixtures containing the doubly labeled $CD_3{}^{18}OH$ nucleophile, the same products display mass spectra characterized by peaks at $m/z = 64$ ($[CH_3C(H)^{18}OCD_3]^+$) and 50 ($[CH_2{}^{18}OCD_3]^+$). No signal was observed with $m/z = 61$ ($[CH_3C(H)^{18}OCH_3]^+$) or $m/z = 47$ ($[CH_2{}^{18}OCH_3]^+$). This result unequivocally excludes the splitting of the CD_3 and ^{18}O markers in any step of the product formation sequences. The recovery of minor amounts of *unlabeled* products from the systems with labeled CH_3OH (Table 1) suggests that other *unlabeled* nucleophiles may take part in the epoxy ring opening. Water is probably the most important, since it is invariably present as ubiquitous impurity either introduced into the mixture together with its bulk components or formed from its radiolysis. Another unlabeled nucleophile in these mixtures is $CH_3{}^{16}OH$ itself, present as an impurity of the starting labeled methanol. Its occurrence is testified by the presence of a minor $m/z = 59$ signal in the *inverted* **2** and **4** from CH_3F systems with labeled methanol as the nucleophile (Table 2).

Mass spectrometric analysis of the products from the $CH_3F/H_2{}^{18}O$ systems reveals the presence of the isotopic signature exclusively at the hydroxy group of *retained* **2** (i.e., the $m/z = 33$ fragment) and at the methoxy group of *inverted* **2** (i.e., the $m/z = 61$ fragment) (Table 2). Besides, detection of a small $m/z = 49$ fragment from *retained* **3**, which is completely absent in the *inverted* enantiomer, indicates that the isotopic signature resides at the methoxy group of *retained* **3**. Observation of an $m/z = 49$ fragment from *retained* **3** and of an $m/z = 61$ signal from *inverted* **2** (Table 2) indicates that the formation process of these products necessarily requires a step where the isotopic marker of $H_2{}^{18}O$ is efficiently incorporated into their methoxy groups. Even in this case, the presence of an $m/z = 31$ signal in the *retained* **2** from $CH_3F/H_2{}^{18}O$ systems is indicative of the concomitant operation of unlabeled water as ubiquitous nucleophilic impurity (Table 2).

Discussion

Reaction Pattern and Stereochemistry: The conditions typical of the present experiments, in particular the low concentration of the starting substrates **1S** and **1R** (<0.65 mol%) diluted in a large excess of the bulk gas (CH_4 or CH_3F), exclude their direct radiolysis as a significant route to the products of Table 1. The presence of an efficient thermal radical scavenger, O_2, inhibits possible free-radical pathways to products in favor of the competing ionic route, the large predominance of which is demonstrated by the marked effect of an ion trap as powerful as $N(CH_3)_3$ on the overall product yield.

γ-Radiolysis of the bulk gas, either CH_4 or CH_3F, generates known yields of the $C_nH_5^+$ ($n = 1, 2$) and $(CH_3)_2F^+$ acids, respectively. These ions are efficiently thermalized by many unreactive collisions with their parent molecules before attacking the nucleophiles present in the mixture, including H_2O. As a consequence, in the CH_4/**1S** (or **1R**)/CH_3OH mixtures, the initially formed $C_nH_5^+$ ($n = 1, 2$) Brønsted acids can attack either the epoxide, yielding the corresponding 1-H-oxonia-2-methyl-cyclopropane derivative (henceforth denoted as H-**1S** (or H-**1R**)), and the added CH_3OH (or the ubiquitous H_2O impurity) yielding eventually the $CH_3OH_2^+$ Brønsted acid. Similarly, in the CH_3F/**1S** (or **1R**)/NuOH (Nu = H or CH_3) systems, the initially formed $(CH_3)_2F^+$ Lewis acid can attack either the epoxide, yielding the corresponding 1-Me-oxonia-2-methylcyclopropane derivative (henceforth named Me-**1S** (or Me-**1R**)),[8] or the added NuOH, giving rise to the corresponding $NuO(H)CH_3^+$ (Nu = H or CH_3) Brønsted acids. Therefore, the nature and the relative distribution of the acidic species generated in the irradiated samples are determined by the nature of the bulk gas and by the presence and the relative concentration of the nucleophiles present in the mixture. In the systems investigated, the $NuO(H)CH_3^+$ (Nu = H or CH_3) acids may exothermically protonate the epoxy substrate, yielding the corresponding oxonium ion H-**1S** (or H-**1R**) ($-\Delta H^\circ = 12.8$ (Nu = H); 2.6 kcal mol^{-1} (Nu = CH_3)).[7] If we make the reasonable assumption that all these processes are highly efficient, it follows that both Me-**1S** (or Me-**1R**) and H-**1S** (or H-**1R**) intermediates are formed in the CH_3F systems, in proportions approximately reflecting those of their ionic precursors $(CH_3)_2F^+$ and $NuO(H)CH_3^+$ (Nu = H or CH_3), respectively.

Both 1-H- (H-**1S** or H-**1R**) and 1-Me-oxonia-2-methylcyclopropanes (Me-**1S** or Me-**1R**), excited by the exothermicity of their formation processes, may in principle undergo unimolecular ring opening and isomerization to the more stable carbonylic structures, unless efficiently quenched by collisions with the bulk gas. However, the exclusive formation of the *inverted* product **2**, coupled with the negligible recovery of the carbonylic isomer of the starting epoxide among the reaction products, demonstrates that excited H-**1S** (or H-**1R**) and Me-**1S** (or Me-**1R**) are rapidly thermalized by multiple collisions with the bulk gas well before any conceivable unimolecular rearrangement takes place. The same evidence indicates that ring opening of H-**1S** (or H-**1R**) and Me-**1S** (or Me-**1R**) necessarily involves nucleophilic attack by NuOH (Nu = H or CH_3). A major difficulty in determining the thermochemistry of these gas-phase reactions arises from the lack of sufficient thermochemical data for the ionic species involved. However, in view of the enthalpy changes involved in the NuOH-induced ring opening of 1-Me-oxoniacyclopropane (ΔH° = ca. -32 (Nu = CH_3) and $+4$ kcal mol^{-1} (Nu = H))[7, 9] and of 1-H-oxoniacyclopropane ($\Delta H^\circ = -21$ (Nu = CH_3) and -7 kcal mol^{-1}(Nu = H)),[7] the same reactions on Me-**1S** (or Me-**1R**) and H-**1S** (or H-**1R**) can be considered as thermodynamically allowed, except perhaps the slightly endothermic ring opening of Me-**1S** (or Me-**1R**) by water.[10] It follows that CH_3OH displacement on H-**1R** (Scheme 2) (and on H-**1R***; vide infra) is the pathway operative in the CH_4/**1R**/CH_3OH mixtures. A similar process is accompanied by another reaction (Scheme 3) in the CH_3F/**1R**/H_2O systems. Both reactions are flanked by a further process (Scheme 4)

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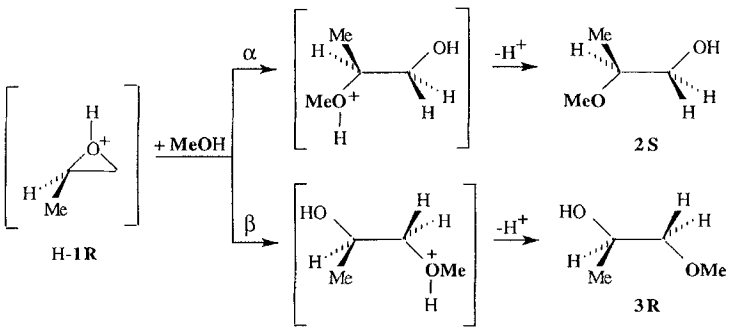
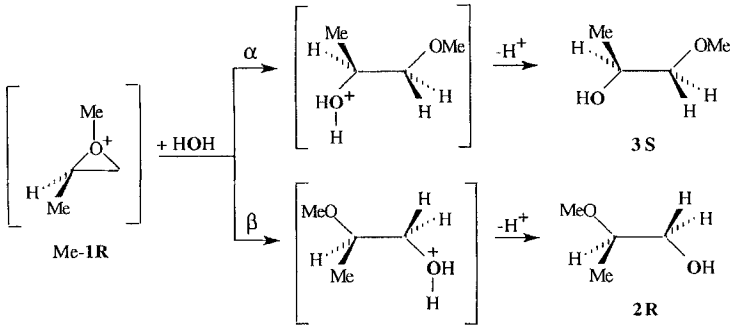
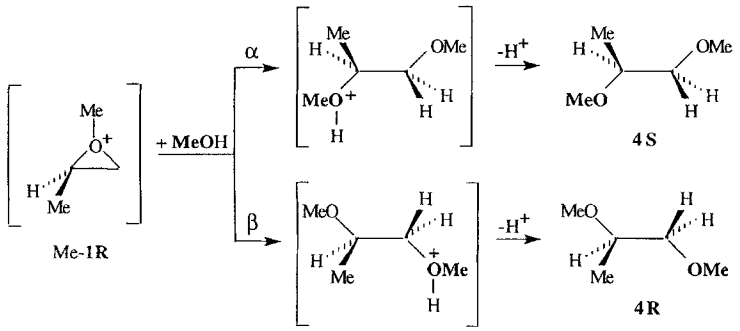


Scheme 2.



Scheme 3.



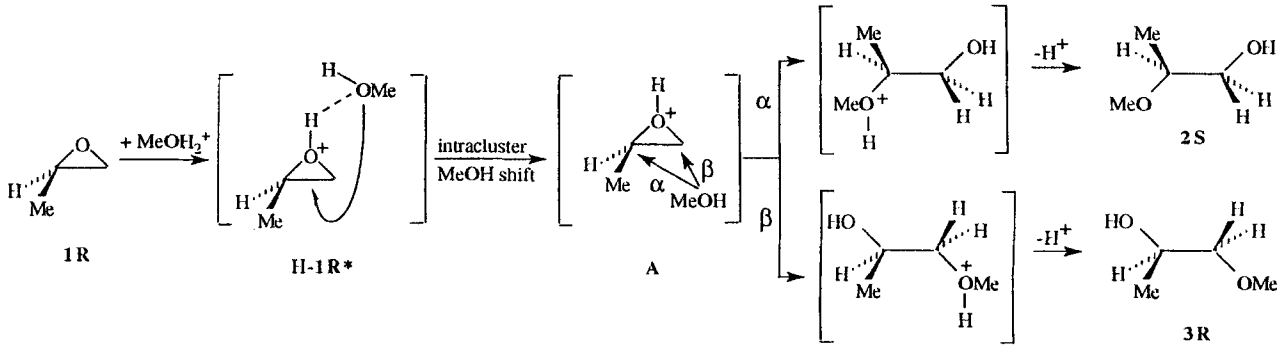
Scheme 4.

in the CH_3F/**1R**/CH_3OH samples. Similar pathways are followed in the corresponding systems with **1S** as the substrate.

Accordingly, in the CH_3F/labeled methanol samples, the exclusive formation of *inverted* **2** and **4**, with the isotopic signature (i.e., the methoxy group) bound to the C2 center, and of *retained* **3** and **4**, with the isotopic signature (i.e., the methoxy group) bound to the C1 position, indicates that the labeled methanol attacks both the Me-substituted (C_α) and the unsubstituted (C_β) carbons of the Me-**1R** (or Me-**1S**) (Scheme 4) and the H-**1R** (or H-**1S**) ions (Scheme 2) and *backside* to their C_α centers. The same regio- and stereoselectivity account for the exclusive formation of *inverted* **2** and *retained* **3** in the CH_4/CH_3OH mixtures through Scheme 2.

In the CH_3F/H_2O systems, the formation of a small yield of *inverted* **3**, with the **HO** group bound to the C2 center, and of *retained* **2**, with the **HO** group bound to the C1 center, suggests the occurrence of the reaction in Scheme 3, involving rearside attack to the ring carbons of the Me-**1R** (or Me-**1S**) intermediates by H_2O. The limited yield of these products ($G(M) = 0.02-0.03$) reflects the inefficiency of the probably slightly endothermic process. Recovery of limited amounts of unlabeled *inverted* **3** and *retained* **2** in the irradiated CH_3F/labeled methanol mixtures is attributed to this slow process, involving the H_2O impurity present in these systems (Table 1).

In the CH_3F/H_2O mixtures, formation of *inverted* **2**, with the CH_3O group bound to the C2 center, and of *retained* **3**, with the CH_3O group bound to the C1 center, is a witness to the action of the Brønsted acid $CH_3OH_2^+$, formed from $(CH_3)_2F^+$-methylation of H_2O, as an additional promoter of the **1R** (or **1S**) ring opening. In this framework, given the enormous excess of the epoxy substrate and of water in these systems relative to *neutral* CH_3OH released by proton transfer from $CH_3OH_2^+$ to the epoxide, the appreciable formation of products containing the OCH_3 group provides compelling evidence for the operation of the *intracomplex* displacement (Scheme 5). The formation of *inverted* **2**, with the CH_3O group bound to the C2 center, and of *retained* **3**, with the CH_3O group bound to the C1 center, without any appreciable contamination from the corresponding enantiomers with the same labeled group, suggests that the CH_3OH moiety, formed after proton transfer from $CH_3OH_2^+$ to the epoxide, *remains coordinated to the H-1R (or H-1S) moiety within the complex H-1R* (or H-1S*) and moves around it to attack the ring carbons from the rearside.* Therefore, the stereoselectivity of the *intracomplex* displacement (Scheme 5) is equal to that of the analogous bimolecular process (Scheme 2) (henceforth denoted as the *extracomplex* pathway).



Scheme 5.

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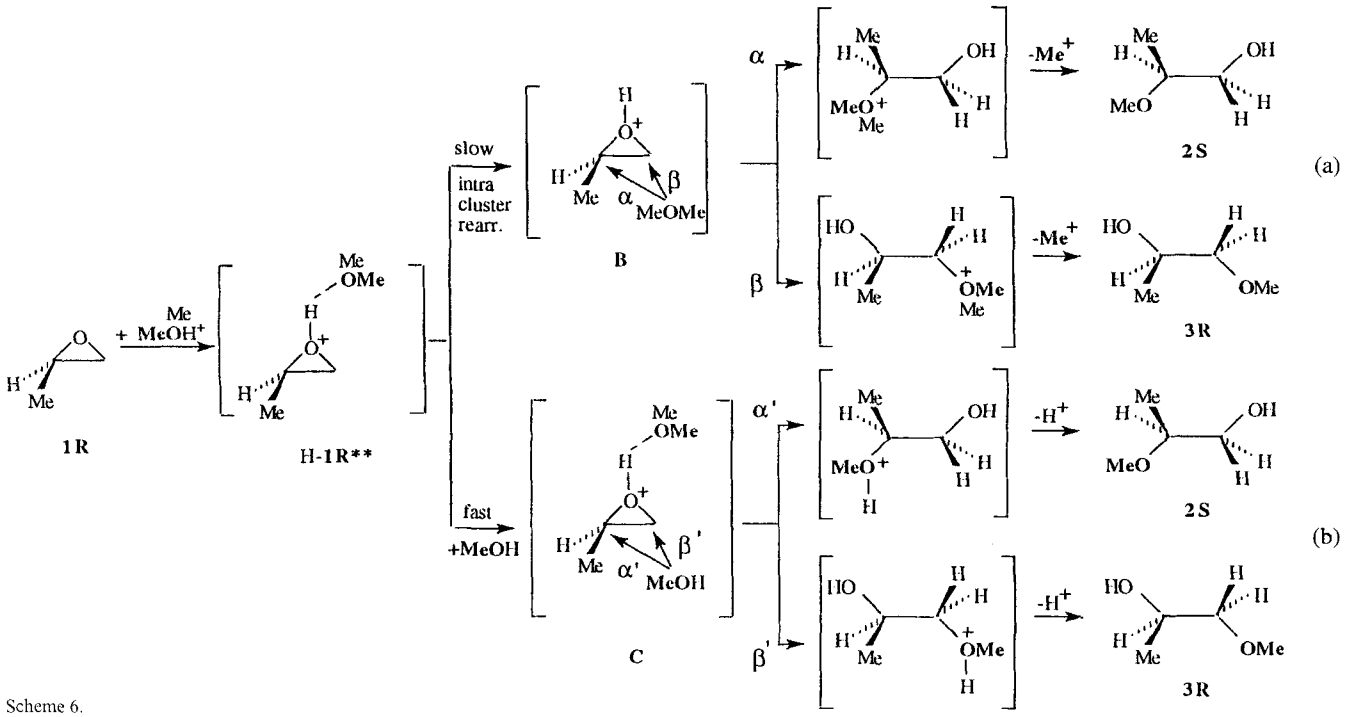
In principle, an *intracomplex* displacement like that in Scheme 5 might also operate in the CH_3F/labeled methanol systems, involving the $NuO(H)CH_3^+$ (Nu = H or CH_3) Brønsted acids (Scheme 6a). However, two pieces of evidence suggest the predominance of the competing *extracomplex* route b (Scheme 6) over the *intracomplex* pathway a in these systems, namely: 1) the absolute yield of the labeled *inverted* **2** and *retained* **3** in the CH_3F/labeled methanol systems, which is about one order of magnitude higher than that measured in the CH_3F/H_2O mixtures; 2) the complete absence of an OCH_3 signature in the *inverted* **2** formed in the CH_3F/**MeOH** systems. Point 1) suggests that the concentration of methanol molecules in the corresponding CH_3F mixtures is sufficient to make the *extracomplex* path b supersede the inefficient *intracomplex* pathway a (Scheme 6). Point 2) further reinforces this view when one considers that, in the frame of an efficient *intracomplex* path a, *inverted* **2** containing the $^{18}OCH_3$ signature would be formed in the $CH_3F/CD_3{}^{18}OH$ systems, in contrast with the experimental evidence. In this view, the *intracomplex* displacement (a) must necessarily involve a sizable activation barrier which exceeds that associated with the nucleophilic displacement step (α or β in Scheme 6a) and can be attributed to the cleavage of the hydrogen bond in H-**1R**** (or H-**1S****) to move the $NuOCH_3$ molecule to the rearside of the oxonium moiety (the H-**1R**** (or H-**1S****) → **B** step in Scheme 6a). Along this line, assuming a unit efficiency for the *extracomplex* displacement b in the CH_3F mixtures with ca. 3 torr of methanol, the timing of the *intracomplex* displacement (Scheme 6a) can be estimated as largely exceeding 10^{-8} s, namely after at least 400 collisions of the H-**1R**** (or H-**1S****) complex with the CH_3F molecules at 720 torr.[11] Thus, it is reasonable to consider these complexes as thermally equilibrated with the bulk gas before rearranging and hence that the *intracomplex* motion of $NuOCH_3$ (Nu = H or CH_3) around the H-**1R** (or H-**1S**) moiety obeys thermal kinetics. Using the typical bond vibration frequency of 10^{13} s^{-1} for the rearrangement preexponential factor, one can estimate the activation barrier of the *intracomplex* motion of $NuOCH_3$ (Nu = H or CH_3) around H-**1R** (or H-**1S**) as exceeding ca. 7 kcal mol^{-1}, which represents a sizable fraction of the proton-bonding energy between the two moieties.[12]

Reaction Regioselectivity: The regioselectivity of the gas-phase nucleophilic ring opening of Me-**1R** (or Me-**1S**) and H-**1R** (or H-**1S**) oxonium intermediates by labeled $NuOCH_3$ (Nu = H or CH_3) (Schemes 3–6) can be easily inferred from the relevant labeled product distributions, reported in parentheses in Table 1. The regioselectivity factors for each individual pathway are listed in Table 3.

Table 3. Regioselectivity of the gas-phase nucleophilic attack of NuOH (Nu = H or Me) on H-**1S**, H-**1R**, Me-**1S**, and Me-**1R**.

Oxonium intermediate	Nucleophile	Mechanism	Regioselectivity, %		α/β ratio
Me-**1S**	H_2O	Scheme 3	81.8 (α)	18.2 (β)	4.48
Me-**1R**	H_2O	Scheme 3	79.1 (α)	20.9 (β)	3.78
					4.13 ± 0.35 [a]
Me-**1S**	MeOH	Scheme 4	70.9 (α)	29.1 (β)	2.44
Me-**1R**	MeOH	Scheme 4	69.9 (α)	30.1 (β)	2.32
Me-**1S**	MeOH	Scheme 4	68.1 (α)	31.9 (β)	2.14
Me-**1R**	MeOH	Scheme 4	68.9 (α)	31.1 (β)	2.21
					2.28 ± 0.16 [a]
H-**1S**	MeOH	Scheme 5	43.3 (α)	56.7 (β)	0.76
H-**1R**	MeOH	Scheme 5	40.3 (α)	59.7 (β)	0.67
					0.71 ± 0.05 [a]
H-**1S**	MeOH	Scheme 6b	43.4 (α)	56.6 (β)	0.77
H-**1R**	MeOH	Scheme 6b	40.5 (α)	59.5 (β)	0.68
H-**1S**	MeOH	Scheme 6b	40.7 (α)	59.3 (β)	0.69
H-**1R**	MeOH	Scheme 6b	42.9 (α)	57.1 (β)	0.75
					0.72 ± 0.05 [a]

[a] Average of the values above.



Scheme 6.

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Analysis reveals an identical regioselectivity for both the *extracomplex* attack of methanol on the C_α and C_β centers of H-**1R**** (or H-**1S****) ($\alpha/\beta = 0.72 \pm 0.05$; Scheme 6b) and the *intracomplex* attack on H-**1R*** (or H-**1S***) by the same nucleophile ($\alpha/\beta = 0.71 \pm 0.05$; Scheme 5), characterized by a slight preference for the C_β center of the corresponding oxonium ion. This observation indicates that both the *intracomplex* and the *extracomplex* reactions involve the intermediacy of a MeOH/oxonium ion adduct, that is, **A** (Scheme 5) and **C** (Scheme 6b), respectively, formation of which is kinetically distinct from the epoxy-ring-opening step and evolution of which to open-chain products is governed by a similar free energy profile. In the *intracomplex* reaction (Scheme 5), cleavage of the proton bond of H-**1R*** to form **A** is the rate-determining step, preceding the fast, product-controlling ring-opening step. However, product-controlling ring opening in **C** is rate-determining in the *extracomplex* reaction (Scheme 6b). Besides, the similar regiochemistry of ring opening in **A** and **C** denotes the relative insensitivity of the nucleophilic displacement to the clustering at the oxygen center of the oxonium moiety by $NuOCH_3$ (Nu = H or CH_3).

The Me-**1R** (or Me-**1S**) intermediate predominantly directs NuOH (Nu = H or CH_3) towards its C_α center ($\alpha/\beta = 4.13 \pm 0.35$ (Nu = H; Scheme 3); $\alpha/\beta = 2.28 \pm 0.16$ (Nu = CH_3; Scheme 4); see Table 3. This preference is a clear symptom of an Me-**1R** (or Me-**1S**) ring-opening transition structure in which the C_α–O bond rupture is significantly more advanced than in the H-**1R** (or H-**1S**) analogues and, therefore, more positive charge is located at the C_α center (a borderline A1–A2 process). In the H-**1R** (or H-**1S**) ring-opening transition structure involved in Schemes 2, 5, and 6b, a more intense interaction with the incoming nucleophile is required to elongate the C–O bonds and, thus, the nucleophilic attack at the less substituted carbon is preferred (an A2 process). Along the same line, the selectivity order toward Me-**1R** (or Me-**1S**) (H_2O $\alpha/\beta = 4.13 \pm 0.35$, Scheme 3; CH_3OH $\alpha/\beta = 2.28 \pm 0.16$, Scheme 4) reflects the degree of C_α–O bond rupture in the corresponding transition structures. According to the thermochemistry, ring opening of Me-**1R** (or Me-**1S**) by H_2O is much less favored than by CH_3OH and, therefore, a more product-like transition structure is involved, characterized by a more significant C_α–O bond elongation.

The regioselectivity of gas-phase methanolysis of H-**1R** (or H-**1S**) displays a very close analogy with that measured for the same reaction carried out in acidic solution, where again an almost indiscriminate nucleophilic attack at both C_α (47.6–49.6%) and C_β (50.4–52.4%) centers of the substrate is observed.[3] Methanolysis of 1,2-epoxypropane in acidic solution proceeds by an A2 mechanism at the C_β center, whereas at the C_α center it follows a borderline A1–A2 mechanism, with bond cleavage being more important than bond formation. The close correspondence between the present gas-phase reactivity and selectivity pattern and those outlined in previous solvolytic investigations provides conclusive evidence that the mechanism, the regiochemistry, and the stereochemistry of the acid-induced ring opening of 1,2-epoxypropane are rather independent of the nature and the solvating power of the solvent and are determined only by the intrinsic structural and electronic properties of the substrate and of the nucleophile.

Conclusions

Application of the well-established radiolytic technique allows investigation of the mechanism and the stereo- and regiochemistry of acid-induced ring opening of optically active 1,2-epoxypropane in the gas phase, interference from bulk solvents and counterions being excluded. The usefulness of this gas-phase approach resides in the unique capability of studying the dependence of the reaction pattern on the nature of the nucleophile and of the acid catalyst under the same experimental conditions. Thus, both the H-**1R** (or H-**1S**) and the Me-**1R** (or Me-**1S**) oxonium intermediates have been conveniently generated under comparable experimental conditions and their ring opening by H_2O and CH_3OH examined. Modulation of the composition of the gaseous mixture allows evaluation of the intrinsic factors governing nucleophilic substitution at H-**1R** (or H-**1S**), which were hardly distinguishable from environmental factors in previous related studies in solution. Thus, depending upon the composition of the gaseous system, two ring-opening mechanisms may take place in the gas phase, one involving an *intracomplex* nucleophilic attack and the other an *extracomplex* substitution by the nucleophile. Both proceed through complete inversion of configuration of the reaction center. The gas-phase *intracomplex* and *extracomplex* reactions display the same regioselectivity, which is comparable to that measured in analogous methanolysis reactions in solution. The different regioselectivity of H-**1R** (or H-**1S**) and the Me-**1R** (or Me-**1S**) toward the selected nucleophiles in the *extracomplex* reaction reflects a transition structure in which C_α–O bond cleavage increases from H-**1R** (or H-**1S**) to Me-**1R** (or Me-**1S**) and in passing from CH_3OH to H_2O.

Experimental Section

Materials: Methane, methyl fluoride, oxygen, and trimethylamine were supplied as high purity gases by Matheson and used without further purification. $H_2{}^{18}O$ ($^{18}O > 97\%$) and CD_3OH (99.8% D) were purchased from Aldrich. $CD_3{}^{18}OH$ (98% D; $^{18}O \approx 98\%$) and $CH_3{}^{18}OH$ ($^{18}O = 95\%$) were obtained from ICON Services. (*S*)-(−)-1,2-Propene oxide (**1S**), (*R*)-(+)-1,2-propene oxide (**1R**), (*S*)-(+)-1,2-propanediol, (*R*)-(−)-1,2-propanediol, (*R*)-(**4R**) and (*S*)-1,2-dimethoxypropane (**4S**) racemate, and (*R*)-(**3R**) and (*S*)-1-methoxy-2-propanol (**3S**) racemate were research grade chemicals from Fluka. The 1,2-dimethoxypropanes enantiomers (**4R** and **4S**), 1-methoxy-2-propanols (**3R** and **3S**), and 2-methoxy-1-propanols (**2R** and **2S**) were synthesized from the corresponding (*R*)-(−)- and (*S*)-(+)-1,2-propanediols through well established procedures and their configuration assigned accordingly.[13]

Procedures: The gaseous mixtures were prepared by conventional techniques; a greaseless vacuum line was used. The reagents and the additives were introduced into carefully degassed 130 mL Pyrex bulbs, each equipped with a break-seal tip. The bulbs were filled with the required mixture of gases, cooled to −196 °C, and sealed. Irradiation was performed at 25 °C in a commercial γ-irradiation facility to a total dose of 2×10^4 Gy at a rate of 3×10^3 Gy h^{-1}, as determined by a neopentane dosimeter. The radiolytic products were analyzed by GLC using a Chrompack CP 9002 gas chromatograph equipped with a flame ionization detector (FID) on a DACTBS-Beta-CDX (30% diacetyl *tert*-butylsilyl-β-cyclodextrin on OV 1701 from MEGA) fused silica column (length 25 m, internal diameter 0.25 mm), operated at 40–120 °C, 3 °min^{-1}. The products were identified by comparison of their retention volumes with those of authentic standard compounds, and their identity checked by GC–mass spectrometry (GC-MS) with a Hewlett-Packard 5890 A gas chromatograph in line with an HP 5970 B mass selective detector. The yields were determined from the areas of the corresponding

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eluted peaks, using the internal standard (3-methyl-3-pentanol) method and individual calibration factors to correct for the detector response. Control experiments were carried out to confirm the lack of undesired thermal ring opening of the 1,2-propene oxide substrates under the irradiation conditions.

Appendix

The relative distribution of the labeled products (reported in parentheses in Table 1) is calculated from the mass spectrometric fragmentation pattern of the relevant products given in Table 2. The extent of labeling ϕ for any given set of products is inferred as follows:

1) $\phi = [m/z = 61 \text{ (or } 62)]/([m/z = 61(\text{or } 62)] + [m/z = 59])$ for the *inverted* 2-methoxy-1-propanol (**2**) and *inverted* 1,2-dimethoxypropane (**4**).
2) $\phi = [m/z = 47(\text{or } 48)]/([m/z = 47(\text{or } 48)] + [m/z = 45])$ for the *retained* **4**.
3) $\phi = [m/z = 33]/([m/z = 33] + [m/z = 31])$ for the *retained* 2-methoxy-1-propanol **2** from the CH_3F/H_2O systems.
4) Determination of ϕ for the 1-methoxy-2-propanol (**3**) requires knowledge of the origin of the $m/z = 45$ fragment, that is, of which fraction can be assigned to $[CH_3CHOH]^+$ and which to $[CH_2OCH_3]^+$. This information can be inferred from the relative abundance of the $m/z = 47$ and $m/z = 45$ fragments measured in the *retained* **3** from the CH_3F/CH_3OH systems, taking their labeling fraction ϕ equal to that of their accompanying *inverted* **2**. Accordingly, the measured $[m/z = 45]/[m/z = 47]$ ratios can be expressed by Equation (1) taking into account that the $[m/z = 45]$ signal arises from both the unlabeled product $(1 - \phi)$ and the $[CH_3CHOH]^+$ fragment of the labeled product ($\phi[CH_3CHOH]^+$), while the $[m/z = 47]$ signal arises from 25% of the unlabeled product ($0.25(1 - \phi)$) (see Results section) and the $[CH_2OCH_3]^+$ fragment of the labeled product ($\phi[CH_2OCH_3]^+$). From Equation (1), $\rho = [CH_2OCH_3]^+/[CH_3CHOH]^+ = 0.45$. By means of this fragmentation ratio, the extent of

$$[m/z = 45]/[m/z = 47] = \{(1 - \phi) + \phi[CH_3CHOH]^+\}/\{\phi[CH_2OCH_3]^+ + 0.25(1 - \phi)\} \quad (1)$$

labeling ϕ in *retained* 1-methoxy-2-propanol (**3**) from the CH_3F/H_2O systems can be calculated by introducing the relevant $[m/z = 45]/[m/z = 47]$ ratios into Equation (1).
5) Similarly, the ϕ factor for *inverted* **3** from the CH_3F/H_2O systems can be calculated from Equation (2) taking into account the fact that the

$$[m/z = 45]/[m/z = 47] = \{(1 - \phi) + \phi[CH_2OCH_3]^+\}/\{\phi[CH_3CHOH]^+ + 0.25\} \quad (2)$$

$[m/z = 45]$ signal represents the unlabeled product $(1 - \phi)$ and the $[CH_2OCH_3]^+$ fragment of the labeled product ($\phi[CH_2OCH_3]^+$), while the $[m/z = 47]$ signal represents 25% of its parent radical ion (0.25) (see footnote [b] of Table 2) and the $[CH_3CHOH]^+$ fragment of the labeled product ($\phi[CH_3CHOH]^+$).
6) $\phi = \{[m/z = 48]\ (1 + \rho)\}/\{[m/z = 45] + [m/z = 48]\}$ for *retained* **3** from the CH_3F/**MeOH** systems.

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