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Anionic Ether Cleavage of Tetrahydrofuran in the Gas Phase

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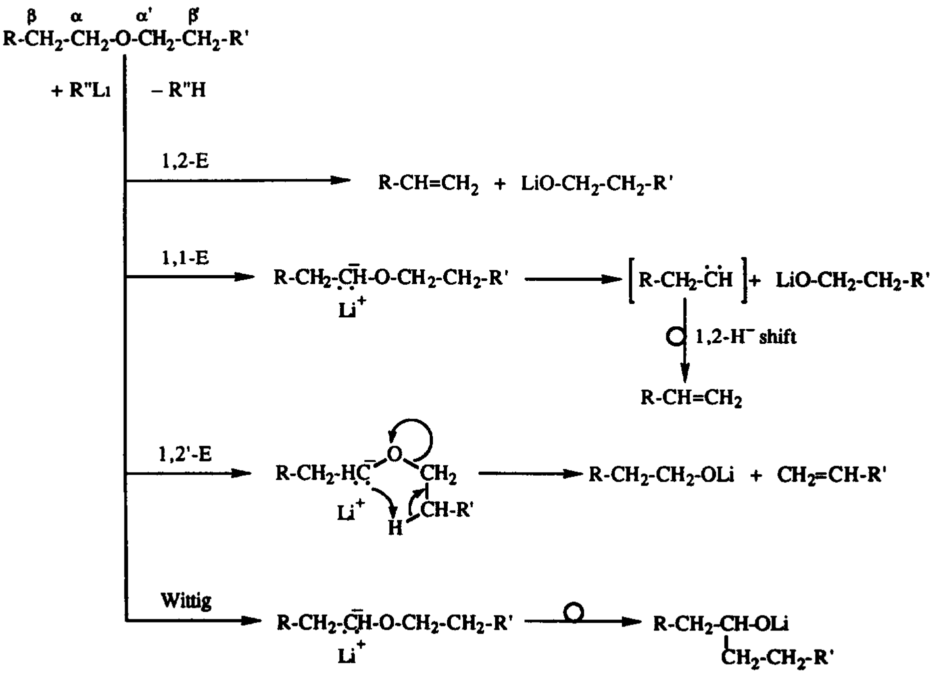
Abstract: The gas phase reactivity of tetrahydofuran (THF) towards a series of anionic bases ($B^- = NH_2^-$, $C_6H_5^-$, OH^-, $CH_2{=}CH{-}CH_2^-$) has been investigated under the low pressure conditions of a Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer.

It appears that under the low pressure conditions the anionic base-induced reactions of THF predominantly proceed by 1,2-elimination. This elimination initially results in rovibrationally excited HB solvated but-3-ene-1-oxide ions. As a result of the absence of thermal interaction with the environment, HB is vaporized from these excited solvated ions. Depending on the nature of the base used, a proportion of the excited but-3-ene-1-oxide is found to eliminate molecular hydrogen or formaldehyde leading to overall exothermic formation of the resonance stabilized buta-1,3-diene-1-oxide ions and allyl anions, respectively.

Interestingly, reaction between the but-3-ene-1-oxide ion and water results in the very efficient formation of hydrated hydroxide ions, [H_2O, OH^-]. Isotopic labeling reveals that formation of this water solvated hydroxide ion is initiated by an endothermic proton transfer from water to but-3-ene-1-oxide which is followed by a reversible hydroxide-induced E1cb process, leading to the elimination of 1,3-butadiene and formation of the hydrated hydroxide ion. To our knowledge, this is the first example of a gas-phase anionic base-induced elimination in which hydroxide is involved as a leaving group.

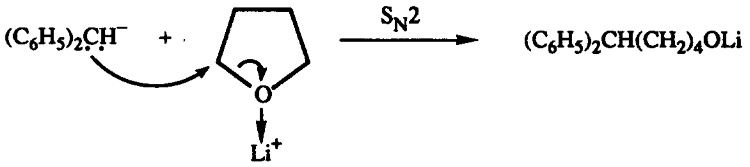
Introduction

Many reactions in synthetic organic chemistry are carried out with ethers as solvents.[1,2] Already for a long time, it has been well known that these solvents are not always inert reaction media as they can undergo anionic ether cleavage. For example, organolithium compounds dissolved in ethers can induce protophilic 1,2-elimination,[3] 1,1-elimination,[4] 1,2'-elimination,[5] and Wittig-rearrangement (Scheme I).[2,5]



Scheme I

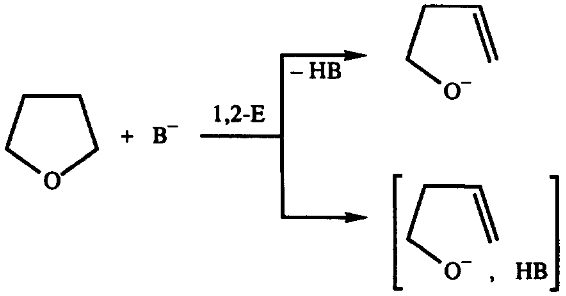
Nucleophilic cleavage is observed in the reaction with soft, resonance stabilized organolithium reagents as for example benzhydryllithium (Equation 1).[2]



(1)

More recently, mechanistic studies on ether cleavage reactions have been performed from which it appears that a specific ether can decompose via different mechanisms.[2] These side reactions can lead to the formation of unexpected products. In some cases, they can be applied in synthesis, and it is important to understand their nature and occurrence.

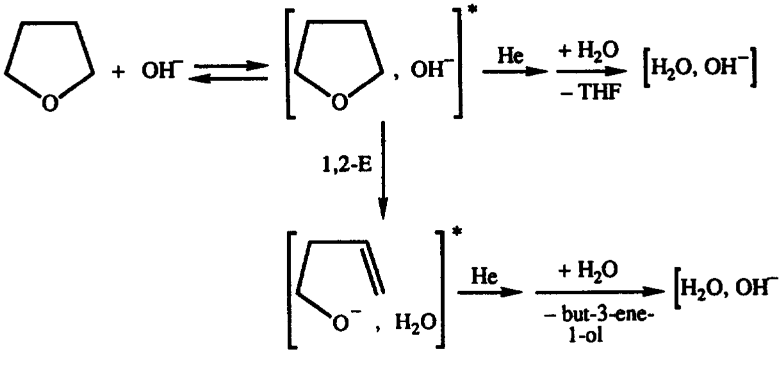
Anionic ether cleavage reactions have also been studied in the gas phase by Ion Cyclotron Resonance (ICR)[6], Flowing Afterglow (FA)[7-10] and Fourier Transform Ion Cyclotron Resonance (FT-ICR)[11] techniques. In general, these studies indicate that base-induced 1,2-elimination reactions strongly prevail in the gas phase. In the studies on the gas-phase anionic base-induced reactions of ethers DePuy, Bierbaum and coworkers have found that under relatively high pressure FA conditions both NH_2^- and OH^- react with tetrahydrofuran (THF) under the competing formation of $(THF\text{–}H)^-$ and $[(THF\text{–}H)^-, HB]$.[8,9] Isotopic labeling has revealed that the formation of these primary product ions proceeds via a 1,2-elimination yielding but-3-ene-1-oxide (Equation 2a) as well as HB solvated but-3-ene-1-oxide ions (Equation 2b).



(2 a)

(2 b)

An interesting phenomenon seems to be the formation of hydrated hydroxide, $[H_2O, OH^-]$, detected as a secondary product ion in the reaction of OH^- and THF.[9] The authors[9] view this formation as a reaction of adventitious water molecules with the collisionally stabilized (by the He carrier gas) loosely bound encounter complex (Equation 3a) or the product complex in which 1,2-elimination has occurred (Equation 3b).



(3 a)

(3 b)

The present study is concerned with the reactivity of THF towards a series of anionic bases (NH_2^-, $C_6H_5^-$, OH^-, $CH_2{=}CH{-}CH_2^-$) under the relatively low pressure FT-ICR[12,13] conditions ($p < 10^{-4}$ Pa) where termolecular reactions and collisional stabilization of intermediate, loosely bound ion/molecule encounter and product complexes are highly restricted. It is the aim of this study to investigate what the effect is of the absence of collisional stabilization of intermediate ion/molecule complexes on the course of the reactions of THF. In particular, it is anticipated that the present study may reveal the origin of the hydrated hydroxide which is observed as a secondary product ion under the relatively high pressure FA conditions.

Experimental

The experiments were performed with a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer constructed at the University of Amsterdam and equipped with a 1.4 T electromagnet and a cubic inch cell (De Koning and Nibbering,[11] and references cited therein). The Segmented Fourier Transform (SEFT) procedure[14] was employed to obtain relative ion abundances with an accuracy of better than 1%. General operating and experimental procedures have been described previously.[11]

The temperature in the cell was around 333 K as measured by a thermocouple on the trapping plate opposite the filament. The total pressure in the different experiments was normally kept below 10^{-4} Pa with a background pressure lower than 5×10^{-7} Pa. The pressure was measured with an ionization gauge placed in a side arm of the main pumping line.

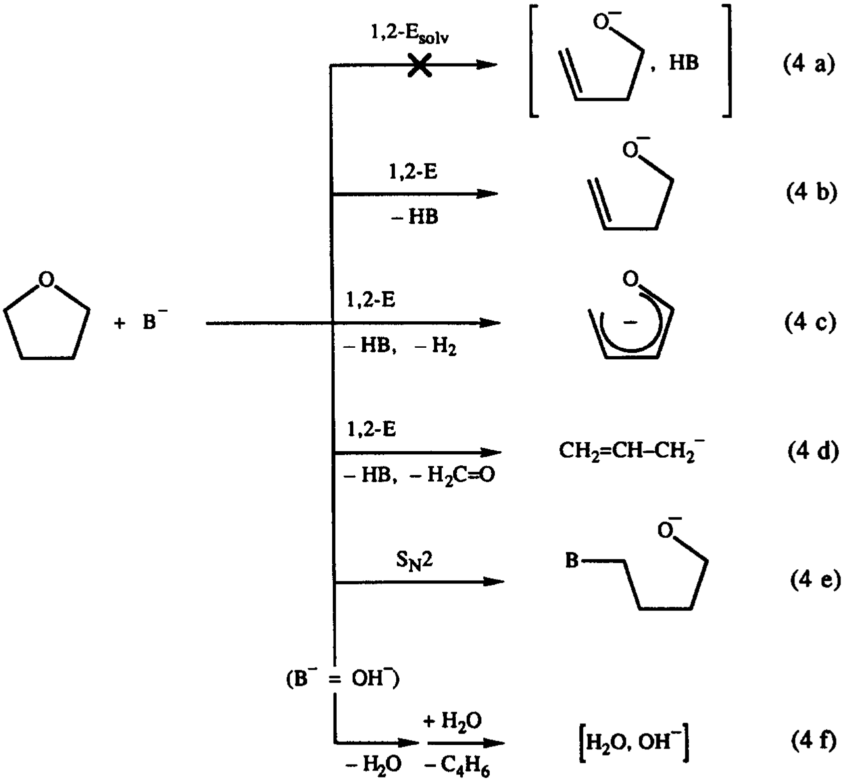
NH_2^- was generated via dissociative resonant capture of electrons with a kinetic energy of 5 eV by NH_3. OH^- was generated via dissociative resonant capture of electrons with a kinetic energy of 6 and 1.5 eV by H_2O (OH^- is formed via H^-) and N_2O (OH^- is formed via $O^{-\bullet}$ and $H^\bullet$ abstraction from the substrate), respectively. The allyl and phenyl anions were produced via proton abstraction by NH_2^- from propene and benzene, respectively. All chemicals were commercially available. The labeling content of $H_2{}^{18}O$ and D_2O amounts to circa 97 % and 94 %, respectively.

Results and Discussion

General

The gas phase reactivity of tetrahydrofuran (THF) towards the anionic bases B^- (B^- = NH_2^-, $C_6H_5^-$, OH^-, $CH_2{=}CH{-}CH_2^-$) has been investigated under relatively low pressure FT-ICR conditions. The experimental results and thermochemical data are summarized in Tables I, II, and III. Table I shows the primary product anion distribution for the reactions of THF with B^-. In the various reactions four types of primary product anions are formed, namely the allyl anion $CH_2{=}CH{-}CH_2^-$, $(THF{-}3H)^-$, $(THF{-}H)^-$, and $(THF{+}B)^-$ (Equation 4b-4e). In the reaction of OH^- with THF, in the presence of gaseous water, the hydrated hydroxide, $[H_2O, OH^-]$, is detected as a secondary product ion (Equation 4f).

All bases studied react with THF under the formation of a $(THF{-}H)^-$ ion (Equation 4b). As in the reactions under FA conditions,[8] the $(THF{-}H)^-$ ion is considered to be formed via a 1,2-elimination reaction in which proton abstraction from the β-position is associated with ring-opening, yielding but-3-ene-1-oxide ions (Equation 4b). Depending on the base used and, in the case of hydroxide, depending on the presence of water molecules in the reaction atmosphere, besides $(THF{-}H)^-$ one of the other above mentioned product anions is formed in the reaction with THF. This is discussed below for the various reaction systems.



The $OH^-/N_2O/THF$ Reaction System

In a water free reaction atmosphere hydroxide reacts with THF under the formation of $(THF–H)^-$ (86%) and $(THF–3H)^-$ (14%; Table I). This is at variance with the FA results[9] which show formation of $(THF–H)^-$ (46%) and $[(THF–H)^-, H_2O]$ (54%), but no formation of $(THF–3H)^-$ ions (Equation 2). This can be rationalized by the absence of "collisional cooling" under the present low pressure conditions, as a result of which the reaction complex is rovibrationally more exited. The energy gained fuels the dissociation of the $[(THF–H)^-, H_2O]^*$ product complex, which cannot be detected (Equation 4a), leading to the formation of the but-3-ene-1-oxide, $(THF–H)^-$, ions (Equation 4b). However, in about 14% of the rovibrationally excited product complexes H_2 is lost from the but-3-ene-1-oxide, $(THF–H)^-$, prior to the

Table I. Primary product ion distributions for reactions of B^- with THF.

B^-	Product anion distribution (%)			
	$CH_2{=}CH{-}CH_2^-$ [a]	$(THF{-}3H)^-$ [b]	$(THF{-}H)^-$ [c]	$(THF{+}B)^-$ [d]
NH_2^-	71	0	29	0
$C_6H_5^-$	0	0	100[e]	0
OH^-	0	14	86	0
$CH_2{=}CH{-}CH_2^-$	0	0	85[e]	15[e]

[a] Equation 4d. [b] Equation 4c. [c] Equation 4b. [d] Equation 4e.

[e] Analysis of primary product ion distribution hampered by the low conversion rate (see text).

Table II. Reaction enthalpies ΔH_r (kcal/mol) associated with reactions of B^- with THF.

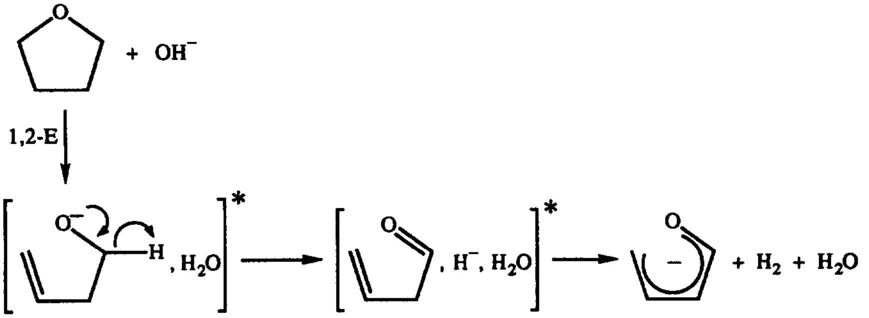
B^-	$PA(B^-)$ [a]	ΔH_r for the formation of [b]			
		$CH_2{=}CH{-}CH_2^-$ [c]	$(THF{-}3H)^-$ [d]	$(THF{-}H)^-$ [e]	$(THF{+}B)^-$ [f]
NH_2^-	403.7	10	−30	−20	−31
$C_6H_5^-$	400.8	13	−27	−17	−40
OH^-	390.8	23	−17	−7	−16
$CH_2{=}CH{-}CH_2^-$	390.8	23	−17	−7	−27

[a] The gas-phase proton affinity (PA) is defined as the enthalpy change associated with the reaction $BH \rightarrow B^- + H^+$ (see reference 15).

[b] Thermochemical data taken from or calculated from heats of formation of Lias et al.[15] or calculated using data from Benson.[23] The PA of $(THF{-}H)^-$ is estimated to equal the PA of n-butoxide (376 kcal/mol).[15] The heat of formation of S_N2 product ions was estimated using the relation $\Delta H_f(B\text{-}(CH_2)_4O^-) \approx \Delta H_f(B\text{-}(CH_2)_4OH)^{23} + PA(n\text{-}BuO^-)^{15,24} - \Delta H_f(H^+)^{15}$

[c] Equation 4d. [d] Equation 4c. [e] Equation 4b. [f] Equation 4e.

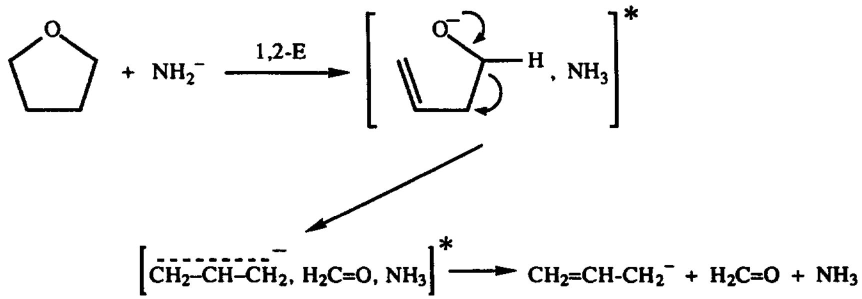
dissociation of the complex leading to the formation of the buta-1,3-diene-1-oxide, $(THF{-}3)^-$, ion (Equation 4c, Table I). The loss of H_2 from rovibrationally exited alkoxide ions is a well known process.[16-18] Formally, the formation of the $(THF{-}3H)^-$ ion can be viewed as initiated by a hydride transfer from the but-3-ene-1-oxide ion to the water molecule resulting in a complex between the hydrated hydride[19] and but-3-enal (Equation 5). Subsequent proton transfer from the but-3-enal ion to the hydrated hydride followed by dissociation of the product complex results in the formation of the strongly resonance stabilized buta-1,3-diene-1-oxide, $(THF{-}3H)^-$, ion. From the data in Table II it follows that formation of the ion is highly exothermic for all the bases used. Nonetheless, only in the reaction induced by OH^- this product ion is detected (Table I). This result shows that the loss of H_2 as represented by the mechanism in Equation 5 is best catalysed by a water molecule in the reaction complex, in agreement with the relatively higher hydride affinity (HA) of water (HA = 16 kcal/mol)[20] relative to, for instance, ammonia (HA = 8 kcal/mol).[20]



(5)

The $NH_2^-/NH_3/THF$ Reaction System

Amide reacts with THF under the present low pressure conditions under formation of $CH_2{=}CH{-}CH_2^-$ (71%) and $(THF{-}H)^-$ (29%; Table I). This is in contrast with the FA results[9] which show formation of $(THF{-}H)^-$ (93%) and $[(THF{-}H)^-, NH_3]$ (7%), but no formation of $CH_2{=}CH{-}CH_2^-$. Again the absence of collisional cooling can be held responsible for the nonappearance of the thermally labile solvated $(THF{-}H)^-$ (Equation 4a). The formation of the allyl anion can be interpreted in terms of a mechanism in which the $(THF{-}H)^-$ ion in the rovibrationally excited product complex $[(THF{-}H)^-, NH_3]^*$ fragments via the alternative pathway as presented in Equation 6. Compared to the situation for hydroxide (ΔH_r = 22.8 kcal/mol) this reaction channel is now considerably less endothermic (ΔH_r = 9.9 kcal/mol; Table II) due to the higher basicity of amide. Nevertheless, the formation of the allyl product anion can only be understood if it is assumed that the reactants are already rovibrationally exited by a few kcal/mol. Apparently, collisional cooling prevents the formation of $CH_2{=}CH{-}CH_2^-$ in the endothermic reaction between NH_2^- and tetrahydrofuran under FA conditions.[9] However, reaction of NH_2^- and the highly strained 2-methyloxetane does lead to the exothermic formation of $CH_2{=}CH{-}CH_2^-$ via an analogous mechanism in which protophilic attack of NH_2^- on the methyl group of 2-methyloxetane induces subsequent 1,2-elimination, ring-opening, and fragmentation.[9,21]



(6)

The $C_6H_5^-/C_6H_6/THF$ and $CH_2{=}CH{\cdot}CH_2^-/CH_2{=}CH{\cdot}CH_3/THF$ Reaction Systems

The reactions of THF induced by the carbon bases appear to be very inefficient, relative to those induced by the nitrogen and oxygen bases. The low conversion rate does not allow for an accurate analysis of the product ion distributions. Yet, it appears that the reaction of the phenyl anion with THF exclusively results in the formation of $(THF{-}H)^-$ ions. However, in the reaction of the allyl anion with THF, both $(THF{-}H)^-$ (85%) and $(THF{+}B)^-$ (15%) have been observed (Table I). In principle, $(THF{+}B)^-$ may be represented by $[(THF{-}H)^-, HB]$ resulting from a 1,2-elimination (Equation 4a). However, this is highly unlikely since no $[(THF{-}H)^-, HB]$ is detected in the reaction of hydroxide with THF, although the 1,2-elimination induced by $CH_2{=}CH{-}CH_2^-$ and OH^- are isoenthalpic (Table II). Moreover, solvation of $(THF{-}H)^-$ by the polar water molecule is probably energetically favored over solvation by the less polar propene. Therefore, the $(THF{+}B)^-$ product ions formed in the reaction induced by $CH_2{=}CH{-}CH_2^-$ can be best represented by $CH_2{=}CH{-}(CH_2)_5{-}O^-$ resulting from a nucleophilic attack of the allyl anion on an α-carbon of THF (S_N2, Equation 4e). It is assumed that this initially rovibrationally excited product ion is thermally less labile than the isomeric [(THF–H)$^-$, CH_2=CH–CH_3] complex ion so that the life-time of this product ion is sufficient to allow collisional stabilization, even under the present low pressure conditions. This gas-phase result parallels condensed phase observations[2] that only soft, resonance stabilized carbanions react with THF via S_N2 substitution.

The inefficiency of proton abstractions from carbon acids by carbanions seems to be a general phenomenon in the gas phase. Representatively, the very inefficient thermoneutral proton transfer from CH_3X (X = Cl, Br) to XCH_2^- is considered to be hindered by a tight transition state which acts as an entropy bottleneck associated with a low density of states.[22] For the allyl anion, the structural change that is caused by the localization of the double bond during the reaction probably enhances this effect.

The Formation of [H_2O, OH^-]

An interesting phenomenon is the efficient formation of the hydrated hydroxide [H_2O, OH^-] when OH^- is allowed to react with THF in the presence of gaseous water, i.e. in the OH^-/H_2O/THF reactant atmosphere rather than in the OH^-/N_2O/THF reactant atmosphere (Equation 4f). The formation of the [H_2O, OH^-] complex is due to a reaction of H_2O and a primary product anion which stems from the reaction between OH^- and THF.The efficient formation of the [H_2O, OH^-] product ions is highly unexpected because the mechanism suggested for the formation of this ion under FA conditions which involves collisional stabilization of the rovibrationally excited intermediate reaction complexes (Equation 3, *vide supra*) is not compatible with the present low pressure conditions. To elucidate the origin of this species, a more detailed mechanistic investigation has been carried out using the technique of oxygen-18 and deuterium isotopic labeling. The experimental results for the various reaction systems are summarized in Table III. Because the secondary reactions involving H_2O are considerably more efficient than the primary reaction between OH^- and THF, determination of the primary product ion distributions for the various reaction systems is hampered. Therefore, Table III shows the product ion distribution at an arbitrary reaction time which is fixed for all reaction systems studied.

Table III. Product anion distributions associated with some reaction systems involving isotopic labeling.[a]

Reaction system	Product anion distribution (%)							
	$D_2HO_2^-$[b]	$D_3O_2^-$[b]	$H_3{}^{18}OO^-$[b]	$H_3{}^{18}O_2^-$[b]	$(THF–3H)^-$	$(THF–4H+D)^-$	$(THF–H)^-$	$(THF–2H+D)^-$
$OH^-/N_2O/THF$	—	—	—	—	18	—	82	—
$^{18}OH^-/H_2{}^{18}O/THF$	—	—	9	43	16	—	32	—
$OD^-/D_2O/THF$	11	59	—	—	5	3	16	6
$(THF–H)^-/D_2O/THF$	38	62	—	—	—	—	c	—
$(THF–3H)^-/D_2O/THF$	—	—	—	—	c	—	—	—

[a] Because an accurate determination of the primary product ion distributions is hampered by the relatively highly efficient secondary reaction between the $(THF–H)^-$ ion and water, the product ion distributions are given at an arbitrary but fixed reaction time for all reaction systems studied.

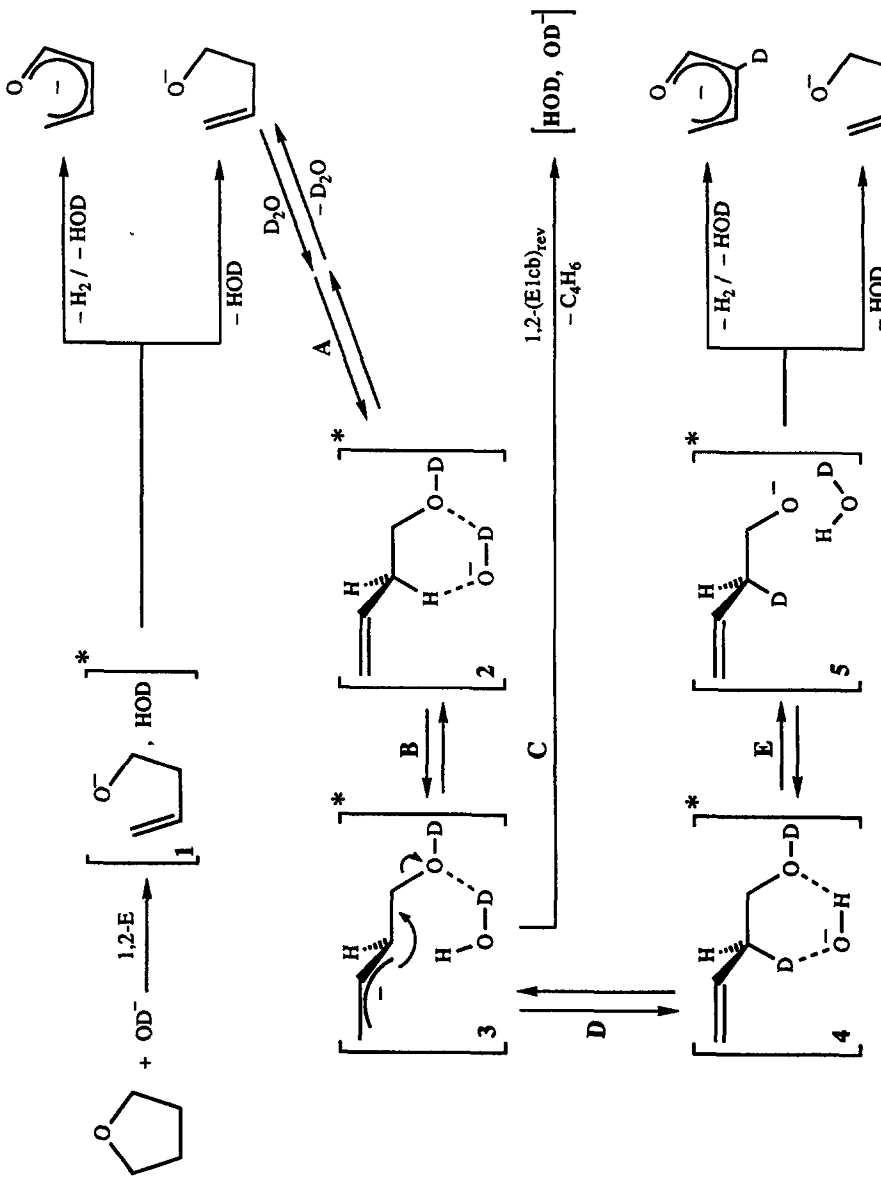
[b] These product ions represent isotopomers of the hydrated hydroxide $[H_2O, OH^-]$.

[c] Reactant ion.

The $^{18}OH^-/H_2{}^{18}O/THF$ and $OD^-/D_2O/THF$ Reaction Systems

The reaction of $^{18}OH^-$ in a $H_2{}^{18}O$/THF atmosphere leads to the formation of $H_3{}^{18}OO^-$ (9%), $H_3{}^{18}O_2{}^-$ (43%), (THF–3H)$^-$ (16%) and (THF–H)$^-$ (32%; Table III). Analogously, the reaction of OD^- in a D_2O/THF atmosphere leads to the formation of $D_2HO_2{}^-$ (11%), $D_3O_2{}^-$ (59%), (THF–3H)$^-$ (5%), (THF–4H+D)$^-$ (3%), (THF–H)$^-$ (16%) and (THF–2H+D)$^-$ (6%; Table III). A mechanism which rationalizes these observations is presented in Scheme II for the OD^-/D_2O/THF reaction system.

As discussed above, the primary (THF–H)$^-$ and (THF–3H)$^-$ ions are generated in an OD^- induced 1,2-elimination reaction of THF. Subsequent association of the but-3-ene-1-oxide, (THF–H)$^-$, ion with D_2O enables an about 15 kcal/mol endothermic deuteron transfer from D_2O to the but-3-ene-1-oxide (reaction step **A**),[15,24] resulting in a hydrogen bound intermediate complex between OD^- and but-3-enol (**2** in Scheme II). Close to thermoneutral proton abstraction from the relatively acidic allylic position of but-3-ene-1-ol by OD^- (reaction step **B**) yields a hydrogen bound intermediate complex between the resulting carbanion and HOD (**3** in Scheme II). HOD assisted cleavage of the C^{α}-OD bond leads to the elimination of 1,3-butadiene from the reaction complex (reaction step **C**) and formation of the observed [HOD, OD^-] product ion. The sequence of reaction steps **B** and **C** can be viewed as a reversible E1cb process, i.e. $(E1cb)_{rev}$. Further, HOD in the [HOD, OD^-] product ion can be exchanged for D_2O which ultimately results in the formation of [D_2O, OD^-]. The above described multi-step reaction between the (THF–H)$^-$ ion and water leading to the formation 1,3-butadiene and the hydrated hydroxide product ion is estimated to be exothermic by 4 kcal/mol.[15,23,24] The analogous formation of the unobserved ammonia solvated hydroxide, [NH_3, OH^-], in the reaction between the (THF–H)$^-$ ion and ammonia (reaction system $NH_2{}^-/NH_3$/THF) involves an about 28 kcal/mol[15,24] endothermic proton transfer from ammonia to (THF–H)$^-$ and is estimated to be overall endothermic by at least 8 kcal/mol.[15,23-25] Evidence for the intermediacy of the complex **3** between HOD and the resonance stabilized carbanion is obtained from the observation of the (THF–4H+D)$^-$ and (THF–2H+D)$^-$ product ions. These product ions can be viewed as the (THF–3H)$^-$ and (THF–H)$^-$ ions in which one deuterium has been incorporated. This incorporation can be considered to proceed via the intermediacy of complex **3** in which H/D exchange occurs between HOD and the resonance stabilized carbanion prior to the reverse reaction back to the reactants involving steps **D** and **E**.


+ OD⁻
1,2-E
1
, HOD
− H₂ / − HOD
− HOD
D₂O
−D₂O
A
2
B
3
C
1,2-(E1cb)rev
− C₄H₆
[HOD, OD⁻]
D
4
E
5
− H₂ / − HOD
− HOD
*

Scheme II

It thus appears that the hydrated hydroxide product ions are generated from a secondary association complex of the $(THF-H)^-$ primary product ions and water and *not* directly from the initial product complex **1** which is composed of the same fragments. This can be rationalized if it is considered that formation of the primary product complex **1** in the hydroxide-induced elimination of THF is more exothermic than formation of this complex via a simple association of the $(THF-H)^-$ product ion and water, because of the energy released in the elimination step (see Table II). As a result, the rovibrationally more excited complex **1** between $(THF-H)^-$ and water formed in the hydroxide-induced elimination of THF rather undergoes a simple entropy favored dissociation than a subsequent reaction towards formation of the hydrated hydroxide ion.

The $(THF-H)^-/D_2O/THF$ and $(THF-3H)^-/D_2O/THF$ Reaction Systems

The but-1,3-diene-1-oxide, $(THF-3H)^-$, ion generated in the hydroxide-induced reaction of THF (Equation 4c) appears to be unreactive in a D_2O/THF atmosphere (Table III). This demonstrates that formation of the $(THF-4H+D)^-$ ion in the $OD^-/D_2O/THF$ reaction system (*vide supra*) is associated with the reaction between the $(THF-H)^-$ ion and D_2O, as suggested in Scheme II, rather than in the reaction between the strongly resonance stabilized $(THF-3H)^-$ ion and D_2O.

The but-3-ene-1-oxide, $(THF-H)^-$, ion, generated in the hydroxide-induced reaction of THF (Equation 4b), very efficiently reacts in the D_2O/THF atmosphere under formation of the isotopomers of the hydrated hydroxide ions (Table III). This clearly shows that these hydrated hydroxide ions result from the reaction between $(THF-H)^-$ and water, as suggested in Scheme II, rather than from the reaction between the hydroxide ion and THF. However, formation of the $(THF-2H+D)^-$, $(THF-4H+D)^-$ and $(THF-3H)^-$ ions observed in the $OD^-/D_2O/THF$ reaction system is not detected in the $(THF-H)^-/D_2O/THF$ reaction system (Table III). This demonstrates that the branching ratio of the elimination of 1,3-butadiene from the intermediate complex **3** in reaction step **C** in Scheme II and the hydrogen/deuterium exchange followed by the reverse reaction leading to incorporation of a deuterium atom in the $(THF-H)^-$ and $(THF-3H)^-$ ions (via reaction steps **D** and **E**) very critically depends on the internal energy of the intermediate complex **3**. Under the low pressure conditions the internal energies of the intermediate complexes are likely to differ slightly for the $(THF-H)^-/D_2O/THF$ and $OD^-/D_2O/THF$ reaction systems.

Conclusions

Under low pressure conditions ($p < 10^{-4}$ Pa) the anionic gas-phase base-induced reactions of tetrahydrofuran (THF) predominantly proceed via 1,2-elimination. This elimination initially results in rovibrationally excited, HB solvated but-3-ene-1-oxide ions. As a result of the absence of thermal interaction with the environment HB is vaporized from these solvated ions. Depending on the nature of the base used, a proportion of the excited but-3-ene-1-oxide ions eliminates molecular hydrogen or formaldehyde leading to the formation of the resonance stabilized but-1,3-diene-1-oxide ions and allyl anions, respectively.

Interestingly, reaction between the but-3-ene-1-oxide ion and water results in the very efficient formation of hydrated hydroxide ions. Isotopic labeling reveals that the formation of this hydrated hydroxide is initiated by an endothermic proton transfer from water to but-3-ene-1-oxide generating a complex between hydroxide and but-3-ene-1-ol. Subsequently, a reversible hydroxide-induced E1cb process leads to the elimination of 1,3-butadiene and formation of the hydrated hydroxide ion. To our knowledge, this is the first example of a gas-phase anionic base-induced elimination in which hydroxide is involved as a leaving group.

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24. The PA of but-3-ene-1-oxide, $CH_2=CH-(CH_2)_2O^-$, and of species $B-(CH_2)_4O^-$ ($B- = NH_2-$, C_6H_5-, $HO-$, $CH_2=CH-CH_2-$) is estimated to equal the PA of n-butoxide (376 kcal/mol).[15]
25. The complexation enthalpy of $[NH_3, OH^-]$ is estimated to be less than or equal to that of $[NH_3, NH_2^-]$ which amounts to −12 kcal/mol.[15]