JOURNAL

OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 104, NUMBER 24 DECEMBER 1, 1982

Reactions of Cyclic Ethers with Amide and Hydroxide Ions in the Gas Phase[†]

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Abstract: The gas-phase reactions of amide and hydroxide ions with a series of ten cyclic ethers have been studied with the flowing afterglow technique. Products and mechanisms were probed by the study of isotopically labeled reactants as well as hydrogen–deuterium exchange reactions. β-Elimination processes dominate, and ring strain and reaction exothermicity are manifested in fragmentations, usually of the reverse-aldol type.

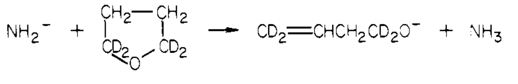
Introduction

The base-promoted bimolecular elimination (E2) reaction in solution has been extensively studied from many standpoints: mechanism, stereochemistry, synthetic applicability.[1] Because so many bonds are formed and broken during the course of the reaction, there are many variables which can influence reaction rates and stereochemistry. Indeed, it has been recognized that the transition state in an E2 reaction is a "variable" one, responding to changes in conditions so as to resemble at one extreme a reaction with a carbanion intermediate (E1CB-like) and at the other extreme a reaction with a carbon cation intermediate (E1-like).[2] The study of the factors influencing E2 reactions in the gas phase presents special problems. With presently available experimental techniques the usual procedure is to examine only the ionic reaction products with a mass spectrometer.[3] In solution most studies have been carried out using halides or tosylates as substrates. In the gas phase if an organic halide is allowed to react with, for example, hydroxide ion, only halide ion is detected; no information is obtained about the neutral product and hence no insight is gained into the direction or stereochemistry of the elimination. While it is true that reaction rate constants can readily be determined for gas-phase ion–molecule reactions, in general these rates tend to be fast and of limited use in elucidating subtle aspects of reaction mechanism.

In order to circumvent some of these problems we have been examining the reactions of ethers with strong bases (NH_2^-, OH^-) in the gas phase. Previously we reported results on elimination reactions of acyclic ethers in which, by examining only the ionic reaction products, we could determine the effects of alkyl substitution on the relative rates of elimination in the two possible directions.[4] We found, for example, that ethyl isopropyl ether reacts with OH^- to give the products shown in eq 1. Several points about the results of the previous investigation are noteworthy. First, in spite of the rapidity of the reactions (over 1 in 10 collisions between ion and neutral result in reaction), the direction of elimination can be extremely selective (for example, 99% of the

$$\begin{aligned} OH^- + CH_3CH_2OCH(CH_3)_2 &\xrightarrow{19\%} CH_3CH_2O^- + H_2O + CH_3CH{=}CH_2 \\ &\xrightarrow{28\%} CH_3CH_2O^-(H_2O) + CH_3CH{=}CH_2 \\ &\xrightarrow{36\%} (CH_3)_2CHO^- + H_2O + CH_2{=}CH_2 \\ &\xrightarrow{17\%} (CH_3)_2CHO^-(H_2O) + CH_2{=}CH_2 \end{aligned} \qquad (1)$$

product of reaction of OH^- with ethyl *tert*-butyl ether results from attack at the *tert*-butyl group). Second, much of the ionic product is formed as an alkoxide-water or alkoxide–ammonia complex rather than as free alkoxide ion. Third, product distributions using amide and hydroxide ion as bases can be interpreted in terms of substituent effects which have their counterparts in the solution chemistry of E2 reactions. Additional information about gas-phase elimination reactions and gas-phase ion–molecule reactions in general can be gained by studying cyclic ethers; with these ethers, elimination results in an ion (M − 1) in which the charge remains attached to the substrate, thus offering the possibility of discovering the fate of the olefinic product. Indeed our studies on one such substrate, 2,2,5,5-tetradeuteriotetrahydrofuran, played a key role in demonstrating that ethers react with strong bases in the gas phase by an E2 process rather than by an S_N2 or proton-abstraction mechanism (eq 2). In this paper we report the products



(2)

of the reactions of a number of cyclic ethers and diethers with amide and hydroxide ions.

[†] Dedicated to Professor William Doering on the occasion of his 65th birthday.

(1) March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977.

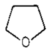
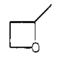
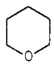
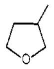
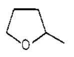
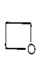
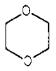
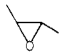
(2) Bunnett, J. F. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 225–235.

(3) Bowers, M. T., Ed. "Gas Phase Ion Chemistry", Academic Press: New York, 1979; Vol. 1 and 2.

(4) DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1981**, *103*, 5034–5038.

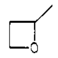
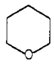
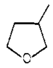
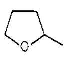
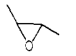
0002-7863/82/1504-6483$01.25/0

Table I. Reactions of NH_2^- and OH^- with Cyclic Ethers

reactant neutral, M		negative ion products	product distributions[a] (%) for $B^- = NH_2^-$	$B^- = OH^-$
1		M − 1	93	46
		M − 1 + BH	7	54
2		M − 1	50	98
		M − 1 + BH	3	2
		$C_3H_5^-$	47	
3		M − 1	92	3
		M − 1 + BH	8	97
4		M − 1	94	45
		M − 1 + BH	6	55
5		M − 1	71	94
		M − 1 + BH	2	6
		$C_2H_3O^-$	27	
6		$C_2H_3O^-$	70	85
		$M + B^-$	trace	15
		$M + B^- - H_2$	30	trace
7		M − 1	78	85
		M − 1 + BH	1	2
		$C_3H_3^-$	21	2
		$C_3H_3^-(BH)$		11
8		$C_2H_3O^-$	100	66
		$C_2H_3O^-(BH)$		34
9		M − 1	14	62
		M − 1 + BH		26
		$C_2H_3O^-$	86	12
10		M − 1	100	100

[a] Product distributions were measured under conditions where mass discrimination is minimized but probably not completely eliminated.

Table II. Rate Constants for Reactions of NH_2^- and OH^-

	NH_2^-	OH^-
	7.6[a]	b
	14	22
	6.6	b
	14	b
	12	2.7
	b	b
	22	30
	1.5[c]	2.5[c]
	12[c]	19[c]
$(C_2H_5)_2O$	4.1[d]	6.1[d]

[a] k in units of 10^{-10} cm^3 molecule^{-1} s^{-1}. The collision rate constants for these reactions are about 2×10^{-9} cm^3 molecule^{-1} s^{-1}; exact values are not listed since the dipole moments and polarizabilities of several of these ethers are unknown. [b] Kinetic measurements were not straightforward; see the discussion in the text. [c] Reference 11. [d] Reference 4.

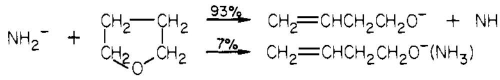
Experimental Section

These experiments were carried out at 298 K with a flowing afterglow apparatus which has been described previously.[5,6] Typical pressures and flow rates of the helium buffer gas were 0.3 torr and 120 STP cm^3 s^{-1}, respectively. Amide ion was generated by electron impact on traces of ammonia while hydroxide was formed by electron impact on a mixture of nitrous oxide and methane. $^{18}OH^-$ was produced from $H_2{}^{18}O$ in the low-pressure ion source of our newly constructed selected ion flow tube.[7] Most ethers were obtained from commercial sources and distilled from lithium aluminum hydride directly into the flowing afterglow. The 2-trideuteriomethyltetrahydrofuran was prepared by lithium aluminum deuteride reduction of ethyl tetrahydrofuroate, conversion of the resulting deuterated tetrahydrofurfuryl alcohol to the tosylate, and further reduction by LiAlD. The resulting compound was purified by gas chromatography. 2-Methyloxetane was synthesized from 1,3-butanediol by a literature procedure.[8]

Results

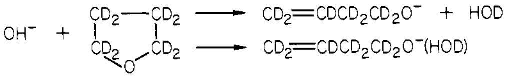
The products formed by reaction of NH_2^- and OH^- with a series of cyclic ethers are summarized in Table I. Table II reports rate constants for some of the reactions investigated together with those for three ethers reported earlier for comparison. The rate constants were measured at 0.3 torr helium pressure by varying the reaction distance for a fixed neutral reactant flow rate; reported values are averages of two or three determinations with different neutral flows. They have a precision of ±10% and a total estimated error of ±30%.

Tetrahydrofuran (1). Tetrahydrofuran (THF) exhibits most of the characteristics of a "standard" gas-phase E2 reaction, and 93% of the product of the reaction with NH_2^- corresponds to M − 1 ions. Since labeling demonstrates that a β proton is lost (eq 2), this is taken as evidence for the operation of an E2 mechanism. The remaining 7% of product ions occurs at M + 16. These ions could correspond to the products of an S_N2 process, but we believe instead that they are cluster ions of the ring-opened alkoxide with NH_3 (eq 3) because (alkoxide + NH_3) ions are also produced (15%) in the reaction of ethyl ether with NH_2^-, and small amounts of analogous ions are formed from all acyclic ethers studied previously. These ions could not be produced by an S_N2 process with an acyclic ether. In addition, we showed earlier that ethers without β hydrogens (e.g., dimethyl or methyl neopentyl ether) do not react with amide or hydroxide ions. Since ammonia is present in the flow tube as the neutral precursor of amide ion, the cluster ions may partially result from termolecular association reactions of the alkoxide with ammonia.



(3)

THF reacts with OH^- to give M − 1 and M + 17 ions which we formulate as the corresponding alkoxide and hydrated alkoxide ions. We demonstrated using THF-d_8 as a substrate that the hydrated alkoxide ion is produced directly in the E2 reaction and not by secondary hydration of the initially formed alkoxide with adventitious water, since the resultant hydrated ion contains HOD (M + 17) as expected by the proposed method of formation (eq 4.) Clustering with water vapor impurities would instead produce M + 16 ions. We believe that the greater amounts of cluster ions formed on reaction of ethers with OH^- than with NH_2^- is due to the greater exothermicity of the latter reaction (13 kcal/mol more exothermic)[9] so that the products dissociate more rapidly, and



(4)

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[5] Ferguson, E. E.; Fehsenfeld, F. C.; Schmeltekopf, A. L. *Adv. At. Mol. Phys.* **1969**, *5*, 1–56.

[6] DePuy, C. H.; Bierbaum, V. M. *Acc. Chem. Res.* **1981**, *14*, 146–153.

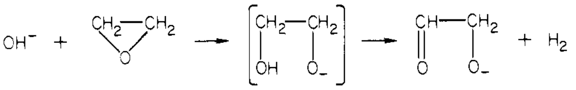
[7] Grabowski, J. J.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.*, in press.

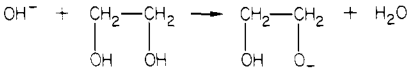
[8] Searles, S.; Pollart, K. A.; Block, F. *J. Am. Chem. Soc.* **1957**, *79*, 952–956.

[9] Bartmess, J. E.; McIver, R. T., Jr., In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, pp 87–121.

because H_2O forms a stronger hydrogen bond to negative ions than does NH_3.[10]

2-Methyloxetane (2). This compound is an isomer of THF and to the extent that elimination is toward the methyl group it should produce the same alkoxide as that formed from THF. However, oxetanes are strained molecules and this strain is relieved upon ring opening. The product ion is thus formed with excess energy which can result in fragmentation. We have previously shown[11] that when the ethylene glycoxide ion is formed by reaction of ethylene oxide with OH^- it fragments (eq 5), but when it is formed by proton abstraction from ethylene glycol it does not (eq 6).


(5)


(6)

$$OH^- + \underset{OH}{CH_2}-\underset{OH}{CH_2} \rightarrow \underset{OH}{CH_2}-\underset{O^-}{CH_2} + H_2O \qquad (6)$$

2-Methyloxetane reacts very rapidly with both OH^- and NH_2^-, in contrast to oxetane itself which reacts only slowly (vide infra). Reaction with OH^- gives the expected two products, alkoxide ion (M − 1) and hydrated alkoxide ion (M + 17). In contrast to the results with THF, however, almost all (98%) of the ions are unhydrated. When amide ion is used as the base, the M − 1 and M + 16 ions make up only 53% of the spectrum; a new ion of m/z 41 accounts for 47% of the products. We formulate this product as the allyl anion, formed by fragmentation of the initially formed alkoxide ion. As evidence that the m/z 41 ion is indeed allyl, we added D_2O downstream and observed up to four H–D exchanges, as expected for this structure.[12]

Tetrahydropyran (3). Tetrahydropyran (THP) reacts with both NH_2^- and OH^- to give products similar to those observed for THF. Amide ion gives M − 1 and M + 16 ions with THP in a ratio similar to that observed for THF. However, OH^- forms significantly more cluster ion (M + 17) with THP than it does with THF. The E2 reaction of THF is almost 5 kcal/mol more exothermic than that of THP, and so these results are consistent with the hypothesis that a more highly exothermic reaction leads to formation of smaller amounts of clustered ion.

3-Methyltetrahydrofuran (4). This isomer of THP reacts with both amide and hydroxide ions to form the expected alkoxide and clustered alkoxide ions.

2-Methyltetrahydrofuran (5). 2-Methyltetrahydrofuran reacts with OH^- to form M − 1 and M + 17 products. The ratios of these peaks (94:6) is higher than that observed for THF itself, but is in the direction expected if a large amount of the product is secondary alkoxide. In acyclic systems secondary alkoxides usually show smaller ratios of hydrated to free ions than do primary alkoxides, because hydrogen bonding is less favorable in the former case. When amide is used as the base, an ion at m/z 43 appears in the spectrum. We formulate this peak as being due to the acetaldehyde enolate ion. The only other ionic products formed are the M − 1 and M + 16 ions.

Oxetane (6). Oxetane reacts only slowly with both NH_2^- and OH^-. With neither base is an M − 1 ion formed except in trace amounts. With amide two ions, one of m/z 43 and one of m/z 72 are the major products. We formulate the former as acetaldehyde enolate and the latter as arising from addition of NH_2^- followed by loss of H_2. With hydroxide ion as the reacting base, acetaldehyde enolate is again the major product, but the adduct M + OH^- (m/z 75) is also produced in appreciable amounts. In its propensity for addition followed by fragmentation as opposed to elimination, oxetane resembles ethylene oxide[11] rather than unstrained cyclic ethers.

Butadiene Monoepoxide (7). This epoxide reacts rapidly with both amide and hydroxide ion mainly by elimination. However, with amide, and to a very small extent with hydroxide, a cleavage reaction occurs to form an ion of m/z 39 which we formulate as the propargyl (allenyl) anion. The structure assigned to this ion is supported by the observation that it exchanges three hydrogens for deuterium upon reaction with D_2O.[12]

1,3-Dioxolane (8). With both amide and hydroxide dioxolane gives elimination and loss of formaldehyde to form the acetaldehyde enolate. Amide gives only the enolate ion while hydroxide gives a mixture of enolate (66%) and the water enolate cluster (34%). Evidence for the structures of these ions comes from their characteristic reactions with D_2O;[12] the enolate ion does not exchange but clusters slowly while the m/z 61 ion is quickly converted to m/z 63. Dioxolane reacts rapidly with both bases.

1,4-Dioxane (9). Acetaldehyde enolate is also a product from the reaction of dioxane with either amide or hydroxide, but in contrast to 1,3-dioxolane, simple elimination is the major product with hydroxide and a sizable product with amide. With hydroxide but not with amide appreciable amounts of cluster ions with the M − 1 ions are also observed. Indeed, 1,4-dioxane is similar to tetrahydropyran in its reaction with hydroxide except for a small channel leading to acetaldehyde enolate.

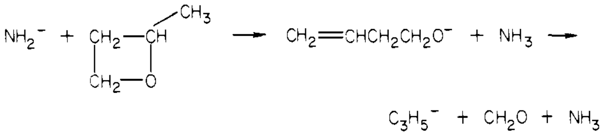
***trans*-2-Butene Oxide (10).** This epoxide reacts with both OH^- and NH_2^- exclusively by elimination to form the unclustered M − 1 ion. Similar behavior had been observed earlier for propylene oxide.[11]

Discussion

These results complement and extend our earlier studies[4,11] on gas-phase reactions of epoxides and acyclic ethers with amide and hydroxide ions. Because the ethers are cyclic, the alkoxide and the olefin are bound together in the product ion. In an exothermic reaction this ion will contain some of the excess energy of reaction, which may fuel an otherwise endothermic fragmentation or be removed by collision with the helium buffer gas. For three of the ethers, tetrahydrofuran (**1**), tetrahydropyran (**3**), and 3-methyltetrahydrofuran (**4**), no low-energy fragmentation pathway apparently exists; these three ethers react with NH_2^- and OH^- to form M − 1 ions as well as M − 1 ions solvated by H_2O or NH_3. These products are those expected by analogy with our studies on acyclic ethers. In addition, we examined *trans*-2-butene oxide for comparison with ethylene oxide and propylene oxide studied earlier; like the latter and in contrast to the former, it undergoes exclusive β-elimination rather than substitution. All the other cyclic ethers studied undergo varying degrees of fragmentation with at least one of the two bases.

2-Methyloxetane (**2**) is a particularly instructive example. It reacts very rapidly with both NH_2^- and OH^-, in contrast to its parent oxetane (**6**) which reacts only slowly with these two bases. With OH^- the M − 1 ion is formed almost exclusively (98%); only a trace of the hydrated alkoxide (M − 1 + H_2O) is produced, in contrast to the large amounts of hydrate formed from the five and six-membered ethers. Elimination undoubtedly occurs by proton loss from the methyl group with ring opening and loss of ring strain. The products are the same as those produced from reaction of OH^- and tetrahydrofuran, but contain an estimated additional 15 kcal of energy. It is not surprising that the product complex separates quickly before it can be stabilized as the hydrate by collision with helium.

2-Methyloxetane (**2**) also reacts very rapidly with NH_2^-. Nearly half (47%) of the ionic products are allyl anions, m/z 41, with the remainder being M − 1 (50%) and M − 1 + NH_3 (3%). No ions of mass 41 are formed by reaction of 2-methyloxetane with hydroxide ion. We believe that these anions result from fragmentation of the initially formed alkene–alkoxide ion to generate formaldehyde and the allyl anions (eq 7).


(7)

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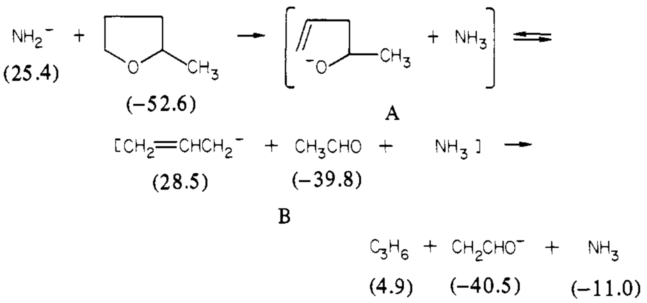
[10] In other experiments we have found that negative ions cluster readily with trace amounts of added water whereas clustering to ammonia is considerably less efficient.

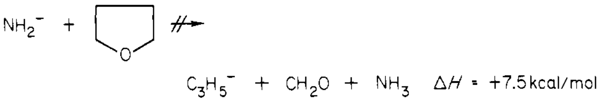
[11] Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H.; Stewart, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4229–4235.

[12] Stewart, J. H.; Shapiro, R. H.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1977**, *99*, 7650–7653.

Scheme I



The observation that the allyl anion is formed by reaction of NH_2^- with 2-methyloxetane but not by reaction of OH^- with the same substrate or by reaction of tetrahydrofuran with NH_2^- is understandable if we examine the thermodynamics of the three processes (eq 8–10).[9,13,14] Only in the latter case is the fragmentation reaction exothermic.



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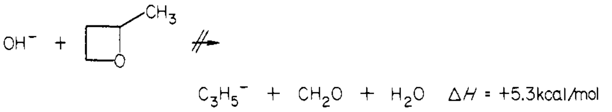

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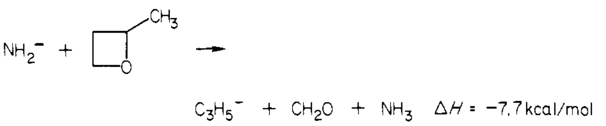
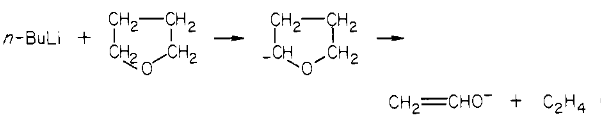


(10)

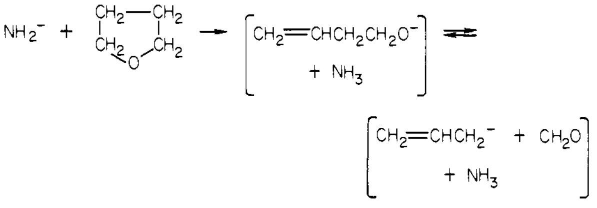
2-Methyltetrahydrofuran (**5**) reacts normally with OH^-, but appreciable amounts of the acetaldehyde enolate ion (*m/z* 43) result from reaction with NH_2^-. In solution THF itself reacts with strong bases to form acetaldehyde enolate by α-deprotonation and cycloreversion (eq 11).[15] However, this mechanism appears unlikely in the gas phase because THF itself does not generate an *m/z* 43 ion. To investigate the source of this ion we used 2-trideuteriomethyltetrahydrofuran as a substrate; the *m/z* 43 peak was replaced by a peak at *m/z* 45. Thus the 2-methyl group is incorporated into the enolate ion.



(11)

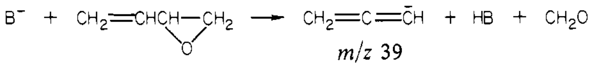
To accommodate these results we propose the mechanism as shown in Scheme I. According to this scheme, amide ion and 2-CH_3-THF are attracted to one another by ion–dipole and ion–induced dipole forces which may amount to 10–15 kcal/mol by the time they reach reaction distance. Elimination results in the formation of the new complex A. Cleavage to the allyl anion and acetaldehyde would be 5 kcal/mol endothermic (ΔH_f° values in kcal/mol are given in parentheses in Scheme I),[9,13,14] but the ion–neutral complex energy makes intermediate B energetically accessible. In this respect the reaction resembles H–D exchange, where an ion–neutral attractive force is presumed to supply energy for proton transfer.[16] Intermediate B may return to A or, by exothermic proton transfer, form acetaldehyde enolate, propylene, and ammonia. The overall process is exothermic by 19.4 kcal/mol. When OH^- rather than NH_2^- is used as the base, the overall process to form acetaldehyde enolate, propylene, and water is still exothermic by 6.4 kcal/mol ($\Delta H_f^\circ(OH^-) = -34.4$ kcal/mol, $\Delta H_f^\circ(H_2O) = -57.8$ kcal/mol). However, even using all of the ion–neutral complex energy, formation of the intermediate complex B with H_2O replacing NH_3 is estimated to be endothermic by at least 3 kcal/mol.

If this mechanism for the formation of the *m/z* 43 ion is correct, it suggests that reversible and hence hidden fragmentation reactions may be occurring in other systems. For example, when THF is allowed to react with NH_2^-, cleavage to the allyl anion and formaldehyde may occur (eq 12). However, since formaldehyde has no acidic α hydrogens to provide another exothermic reaction channel, recombination to the alkoxide will take place. This hidden fragmentation, if indeed it occurs, would have no observable consequences in the case of THF itself. But since recombination could occur at either end of the allylic system, it provides a pathway for an unexpected rearrangement of the product ion and may have consequences in other systems.



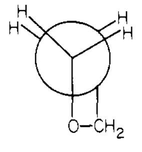
(12)

The monoepoxide of butadiene (**7**) provides a related example of a cyclic ether which undergoes fragmentation upon ring opening. In this case cleavage is observed with both NH_2^- and OH^- as base. The resultant allenyl anion is significantly less basic than the allyl anion formed from 2-methyloxetane, and hence may be formed by reaction with either base. The exothermicity of eq 13 is estimated to be 18 kcal/mol when NH_2^- is the reactant base and 5 kcal/mol for OH^-. In the reaction of OH^-, however, 11% of the product corresponds to $C_3H_3^-(H_2O)$, representing incomplete dissociation of the reaction intermediate.



(13)

Oxetane (**6**) reveals still another type of fragmentation process. Reaction is slow with both NH_2^- and OH^-, and no M − 1 ions are formed with either base. Evidently oxetane, like ethylene oxide and in contrast to all other ethers studied, prefers to react by substitution rather than elimination. These results offer the first hint that gas-phase E2 reactions, like those in solution, are under strong stereoelectronic control. When the leaving group (O^-) is incorporated into a small ring, the β hydrogen which must be removed in an elimination cannot become antiperiplanar. The lack of E2 reactivity of oxetane and ethylene oxide suggest that this stereochemistry is important. Of course a syn-periplanar stereochemistry for the β hydrogen and the leaving O^- is also impossible in oxetane and ethylene oxide, but this stereochemistry is also impossible for THF and THP, which do eliminate. It appears likely from these contrasting results that gas-phase E2 reactions of ethers prefer transition states in which the oxygen and the β-hydrogen are at least close to antiperiplanar.



Oxetane reacts with OH^- by substitution (15%) and substitution followed by fragmentation (85%). The results with oxetane have led us to reformulate our mechanism for the reaction of ethylene oxide with OH^- and NH_2^-. We originally proposed that ethylene oxide undergoes substitution followed by loss of H_2 across the newly formed C–O bond (eq 5). An analogous mechanism could account for the products of the reaction of OH^- with oxetane (eq

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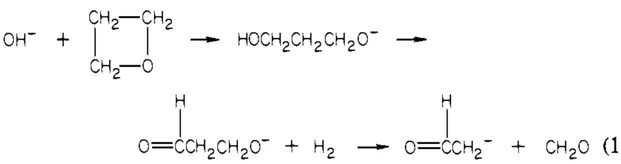
(13) Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K.; Field, F. H. "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions"; NSRDS-NBS 26, U.S. Government Printing Office, Washington, D.C. 1969.

(14) Benson, S. W. "Thermochemical Kinetics," 2nd ed.; Wiley: New York, 1976.

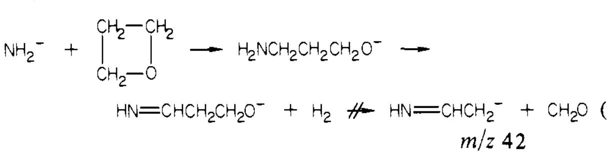
(15) Bates, R. B.; Kroposki, L. M.; Potter, D. E. *J. Org. Chem.* **1972**, *37*, 560–562.

(16) Squires, R. R.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1981**, *103*, 4256–4258.

14). However, this mechanism for the reaction of NH_2^- with

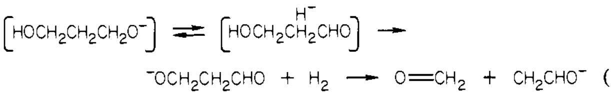

(14)

oxetane predicts the formation of the acetaldehyde imine anion (*m/z* 42) (eq 15). Instead, acetaldehyde enolate (*m/z* 43) is again

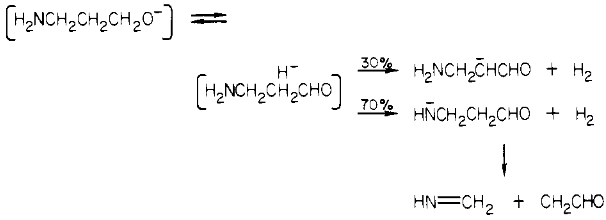

(15)

the major product. This observation rules out simple H_2 loss across the newly formed bond in this case, and led us to search for a mechanism which would be applicable to all four reactions, i.e., reactions of ethylene oxide and oxetane with amide and hydroxide ions.

If reversible cleavage to a carbonyl group and a carbanion is possible even for unstrained molecules like 2-methyltetrahydrofuran upon reaction with strong base, a similar cleavage to a carbonyl group and hydride ion might well occur in the highly exothermic reaction of strained ethers. In the case of reaction of OH^-, the hydride ion would be expected to react rapidly with the proton of the alcohol group to form H_2 and an alkoxide ion, which can cleave to the observed enolate (eq 16).

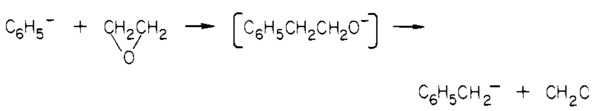

(16)

For reactions with NH_2^-, reaction of the proton on the amine would be expected to be less rapid, since primary amines have about the same acidity as hydrogen. There could then be a competition between proton abstraction from the α carbon and from the amine group, as shown in eq 17.


(17)

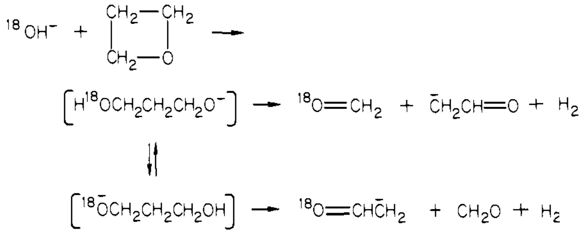
A similar loss of H^- from the initially formed adduct between ethylene oxide and OH^- or NH_2^- could also be invoked to account for the observed products of these reactions. These pathways have the advantage that they do not require us to postulate an orbital symmetry-forbidden 2 + 2 cycloreversion, as we must in the previously suggested mechanism.

We do not consider this fragmentation to H^- to be proven, but the conversion of reaction exothermicity into fragmentation is certainly a reasonable postulate. In order to examine this pathway further we studied the reaction between ethylene oxide and phenide ion (eq 18). Addition leads, in a highly exothermic reaction, to


(18)

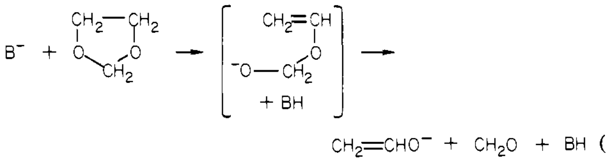
the β-phenylethoxide ion; a simple adduct is not seen and the benzyl anion, formed by loss of formaldehyde, is the sole product. This cleavage is quite analogous to the more endothermic ones postulated for reactions with NH_2^- and OH^-. In these cases, however, the reactions are driven to products by formation of H_2, just as the cleavage of the anion from 2-methyltetrahydrofuran is driven by the formation of acetaldehyde enolate.

The observation of an adduct ion from reaction of oxetane and OH^-, albeit in small amounts, suggested that the intermediate alkoxide anion has a relatively long lifetime, long enough to be stabilized by collision with helium. If this is so there should be time for equilibration of the proton between the two oxygen atoms before fragmentation. To test for this we allowed oxetane to react with labeled hydroxide ions and found indeed an equal mixture of *m/z* 43 and *m/z* 45 ions. This observation also serves to rule

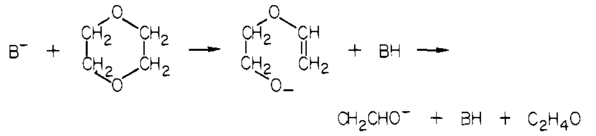

(19)

out some other, more exotic mechanisms for the production of the *m/z* 43 ions from oxetane.

Finally, we examined two cyclic diethers, 1,3-dioxolane and 1,4-dioxane. Both compounds reacted rapidly with OH^- and NH_2^-. 1,3-Dioxolane undergoes exclusively elimination and loss of formaldehyde (eq 20).


(20)

1,4-Dioxane undergoes simple elimination as well as elimination and loss of acetaldehyde (eq 21).


(21)

The loss of acetaldehyde could involve a second elimination reaction occurring within the initially formed complex, or could involve a cyclic proton transfer. As expected, considerably more fragmentation occurs in the more highly exothermic reaction with NH_2^-. Bartmess et al.[17] have studied elimination, fragmentation, and proton-transfer reactions in 1,3-dithianes and 1,3-dithiolanes in an ion cyclotron resonance spectrometer. They also investigated the reactions of methoxide with 1,3-dioxolane and 1,3-dioxane; in the former, they observed formation of the acetaldehyde anion (in analogy with eq 20) as well as unfragmented M − 1 anion. The occurrence of less fragmentation in the reaction of methoxide relative to amide and hydroxide presumably arises from the lower exothermicity. The reaction of methoxide with 1,3-dioxane forms only the M − 1 anion in contrast to our results for 1,4-dioxane.

Rates of Elimination

The reactions of amide ion and hydroxide ion are facile with most cyclic and acyclic ethers containing β-hydrogen atoms, usually proceeding at 10% or greater of the collision rate. As summarized in Table II, hydroxide ion reacts more rapidly than amide with 2-methyloxetane (**2**), *trans*-2-butene oxide (**10**), ethylene oxide, propylene oxide, and diethyl ether. This higher reactivity of the weaker base is not uncommon for fast reactions but the origin of the effect is not understood. However, in 2-methyltetrahydrofuran (**5**) the trend is reversed. For this neutral, reaction of amide apparently occurs both on the substituent and on the ring since reaction of NH_2^- with unsubstituted tetrahydrofuran (**1**) is facile; in contrast, direct attack on the ring by OH^- is apparently slow.

The kinetics of reaction of OH^- with tetrahydrofuran (**1**), tetrahydropyran (**3**), 3-methyltetrahydrofuran (**4**), and oxetane (**6**) exhibit unusual behavior. As the flow of organic reactant or

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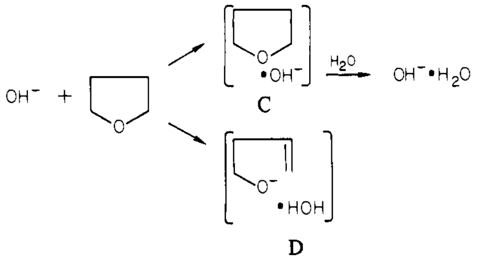
[17] Bartmess, J. E.; Hays, R. L.; Khatri, H. N.; Misra, R. N.; Wilson, S. R. *J. Am. Chem. Soc.* **1981**, *103*, 4746–4751.

6488 *J. Am. Chem. Soc.* **1982**, *104*, 6488-6493

the reaction time was increased, the detected OH^- current initially increased substantially before beginning to decrease. For all of these reactions, a major ionic product appeared at a mass corresponding to addition of the reactants. These products are rapidly destroyed by traces of water vapor, carbon dioxide, or other impurities to produce $OH^-(H_2O)$, HCO_3^-, or other corresponding species. We view this process as occurring by the mechanism in eq 22. The adduct (most likely a simple cluster C but conceivably



(22)

a cluster D in which elimination has occurred) is weakly bound, and a large fraction of these species collisionally dissociate to regenerate reactants. This phenomenon produces an increase in detected OH^- signal since the more rapidly diffusing OH^- species is temporarily replaced in the flow tube by a larger, more slowly diffusing adduct; the diffusive loss of ions is thereby lessened.[18] Addition of water rapidly and quantitatively destroys the adducts. There is evidence that at least some of the addition product exists in form D. When OH^- is allowed to react with perdeuteriotetrahydrofuran, both OD^- and $OD^-(H_2O)$ are generated; these species must originate from decomposition and a switching reaction, respectively, of complex D in which elimination has occurred.

Similar unusual kinetic behavior occurs for reaction of NH_2^- with oxetane, and a mechanism similar to eq 22 is therefore implicated. The adduct in this case is expected to be very weakly bound, and, in fact, only traces of this ion are observed. Alternatively, for oxetane the initial substitution product $[H_2NCH_2CH_2CH_2O^-]$ may fragment by an exothermic but "invisible" process

$$[H_2NCH_2CH_2CH_2O^-] \rightarrow NH_2^- + CH_2CH_2 + CH_2O \qquad (23)$$

This mechanism would also explain the slow rates of reaction of NH_2^- and OH^- with oxetane.[19] The reactions of amide with tetrahydrofuran, tetrahydropyran, and 3-methyltetrahydrofuran, in contrast to those of hydroxide, are well behaved and easily measured and only small amounts of adduct formation are observed.

In conclusion we have observed that most cyclic ethers undergo rapid β-elimination reactions with NH_2^- and OH^- in the gas phase. Strained ethers which react by ring opening may generate ions with sufficient internal energy to allow further fragmentation, usually of the reverse-aldol type. Indeed, even unstrained ethers may fragment upon ring opening, and reversible, and hence hidden, fragmentation may be a common phenomenon in gas-phase reactions of anions.

Acknowledgment. We gratefully acknowledge support of the National Science Foundation under Grant CHE79-09750. We thank Mr. Joseph J. Grabowski for carrying out the reaction of $^{18}OH^-$ with oxetane.

Registry No. 1, 109-99-9; **2**, 2167-39-7; **3**, 142-68-7; **4**, 13423-15-9; **5**, 96-47-9; **6**, 503-30-0; **7**, 930-22-3; **8**, 646-06-0; 9, 123-91-1; **10**, 21490-63-1; NH_2^-, 17655-31-1; OH^-, 14280-30-9.

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(18) For a discussion of the effect of diffusive loss of ions on flowing afterglow measurements, see: Streit, G. E.; Newton, T. W. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *38*, 105-126. Bierbaum, V. M.; Golde, M. F.; Kaufman, F. *J. Chem. Phys.* **1976**, *65*, 2715-2724. Fehsenfeld, F. C.; Howard, C. J.; Schmeltekopf, A. L. *J. Chem. Phys.* **1975**, *63*, 2835-2841.

(19) We acknowledge the suggestion of this mechanism by a referee.

Long-Distance Fluorescence Quenching by Electron Transfer in Rigid Solutions[1]

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Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439. *Received March 22, 1982*

Abstract: Fluorescence of aromatic molecules in solid solutions at room temperature and low temperature is quenched by addition of strong electron donors. The efficiency of quenching correlates well with calculated energetics for electron transfer (ET) from the added donors to the excited molecules, $D + A^* \rightarrow D^+ + A^-$. The quencher (D) always had a substantially higher-lying excited state than did A to prevent electronic energy transfer (e.g., Förster transfer). The A* fluorescence decreased exponentially with D concentration, being halved by addition of about 0.1 M D in cases with favorable energetics for electron transfer. These quenching measurements are interpreted as indicating electron transfer over distances up to 15 Å (center to center). These maximum quenching distances are in excellent agreement with electron tunneling distances measured for ion-molecule reactions by pulse radiolysis. Formation of donor-acceptor complexes during sample preparation is a possible alternate interpretation, but several features of the data provide evidence against this alternative.

Introduction

Intermolecular electron transfer (ET) has long been recognized as an efficient mechanism for fluorescence quenching in fluid solutions.[4-9] The energetics of the ET steps can be described in terms of the singlet excitation energy ($E(S_1)$) of the excited molecule, the oxidation potential ($E(D/D^+)$) of the donor (D),

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(1) Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, U.S. Department of Energy, under Contract Number W-31-109-ENG-38.

(2) Undergraduate Research Participant from Kent State University. The work was performed at Argonne under a program administered by the Argonne Division of Educational Programs and supported by the U.S. Department of Energy, Office of Energy Research, through its University/National Laboratory Cooperative Program.

(3) Undergraduate Research Participant from the University of Chicago; see note 2.

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(6) See also earlier references cited in ref 4 and 5.

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(8) L. V. Romonshov, Y. I. Kiryakin, and K. S. Bagdasar'yan, *Dokl. Phys. Chem. (Engl. Transl.)*, **230**, 961 (1976).

(9) E. Vogelmann, S. Schreiner, W. Rauscher, and H. Kramer, *Z. Phys. Chem. (Frankfurt am Main)*, **101**, 321-6 (1976); S. Tamura, K. Kikuchi, H. Kukubun, and Y. Usui, *ibid.*, **111**, 7-18 (1978).

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