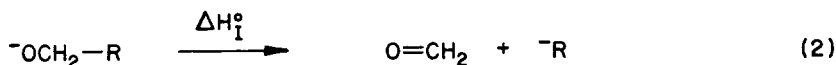
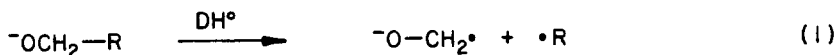


INTRINSIC FRAGMENTATION MODES OF PRIMARY ALKOXIDES

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In the previous communication we have provided thermochemical estimates on the perturbation of negatively charged oxygen on bond homolysis (eq. 1).¹ The purpose of this communication is to compare the energetics of gas phase homolysis (eq. 1) with that of heterolysis (eq. 2), and to correlate these results with analogous processes in solution where metal counterions are known to play an important role in the mode of alkoxide fragmentation.

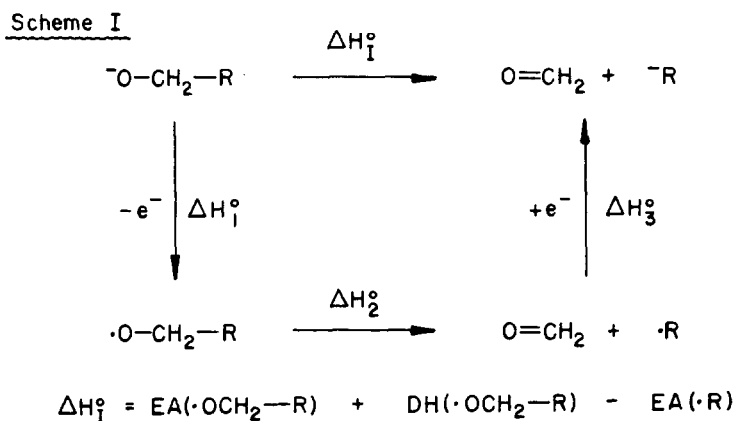


Alkoxide fragmentation processes, both in solution²⁻⁷ and in the gas phase,³ have been reported by several investigators. From these studies the fragmentation mode (homolysis vs. heterolysis) appears to be defined not only by substrate alkoxide but also by counterion and solvent. In a classic study Cram demonstrated the importance of alkali metal counterions in dictating the course of alkoxide fragmentation via heterolytic or homolytic modes. In the case of substrate 1 (M = K, Na, Li), predominant heterolysis (eq. 2) was observed for M = K while homolysis (eq. 1) was preferred for M = Li.⁵

	M	$k_{\text{het}} / k_{\text{hom}}$
$\begin{array}{c} \text{Ph} \quad \text{CH}_3 \\ \quad \\ \text{MO}-\text{C}=\text{C}-\text{Ph} \\ \quad \\ \text{Ph} \quad \text{C}_2\text{H}_5 \end{array}$	K	2.2
	Na	1.6
	Li	0.05

1

In conjunction with our studies on alkoxide-promoted molecular rearrangements, we have determined the intrinsic reactivity of alkoxides in the absence of metal counterion and solvent effects by estimating the gas phase enthalpies of reaction for the two fragmentation modes, radical (DH°) and ionic (ΔH_1°). Calculation of these energies is only possible for primary alkoxides due to the limited availability of relevant thermochemical data at the present time. In principle, however, this approach can be generalized to include the fragmentation of more highly substituted alkoxides. Analogous to the procedure for estimating bond dissociation energies, the enthalpy for the ionic fragmentation process (eq. 2) can be derived from the thermochemical cycle illustrated in Scheme I by employing known electron affinities (EA) and bond strengths.^{1,8} The results are summarized in Table I.



In the absence of the moderating influence of both metal counterion and solvent, heterolysis of methoxide, ethoxide and 3-butenoxide is favored over homolysis by 34, 17, and 28 kcal/mol respectively. The preference for bond heterolysis in free alkoxides agrees with Cram's observation on the counterion dependent cleavage of 1 in solution.⁵ Recently, Arnett and McIver³ have reported the fragmentation of the potassium salt of tri-tert-butylcarbinol in solution (25°C, DMSO). Due to the absence of radical coupling products, they concluded that alkoxide decomposition was probably proceeding via heterolytic rather than homolytic cleavage, although the latter process couldn't be ruled out. Our thermochemical estimates for DH° and ΔH_1° for primary alkoxides lend support to the above conclusions. At the present time thermochemical data is not available on the effect of metal cations, M^+ , on $\text{DH}^\circ(\text{MOCH}_2\text{---R})$ and $\Delta\text{H}_1^\circ(\text{MOCH}_2\text{---R})$. However, both DH° and ΔH_1° values should increase, but by differing increments, as the donor properties of oxygen are curtailed by ion pairing to increasingly electronegative metal counterions. As suggested by Cram's study,⁵ bond homolysis may well be preferred in many lithium and magnesium alkoxides.

Table I. Calculated Fragmentation Energies for
Primary Alkoxides, $^-\text{OCH}_2\text{-R}^{\text{a,b}}$

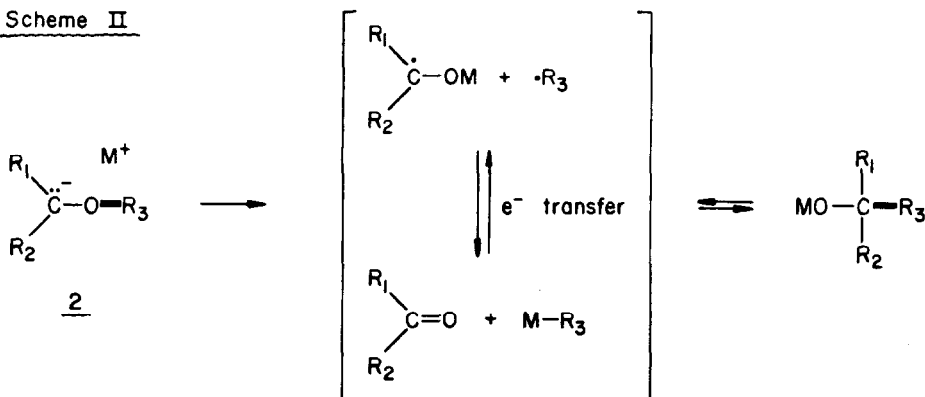
<u>R</u>	<u>DH°($\bar{\text{O}}\text{CH}_2\text{-R}$)^c</u>	<u>ΔH_1°</u>
H	76	42
CH ₃	68	51
CH ₂ CH=CH ₂	58	30

^aAll values reported in kcal/mol. ^bGas phase, 298°K.

^cRef. 1.

Mechanistically, alkoxide fragmentations such as those discussed above bear a striking resemblance to the well-known Wittig rearrangement of metallated ethers 2 (Scheme II).¹² Homolytic as well as heterolytic dissociation modes of 2 have been intensively examined mechanistic issues. Recent studies have provided evidence for radical pair intermediates in this [1,2] sigmatropic process.¹² In the Wittig rearrangement the charged carbon donor substituent which facilitates carbon-oxygen bond homolysis is subject to counterion effects similar to that found in alkoxide fragmentation.^{12,13} Thus, dissociated metal alkyls undergo rearrangement while covalent metal alkyls do not. Finally, the radical and/or

Scheme II



charged intermediates accessible from metallated ethers or alkoxides are simply related by an electron transfer process. This corresponds to the single electron transfer (SET) mechanism proposed by Ashby for the addition of organometallics to carbonyl compounds.¹⁴ Accordingly, those factors identified by Ashby which favor the SET mechanism in organometallic-carbonyl addition should be relevant to defining the course of alkoxide fragmentation.

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