# ALKOXIDE SUBSTITUENT EFFECTS ON CARBON-CARBON
BOND HOMOLYSIS
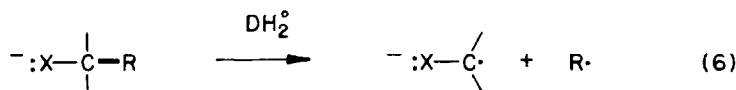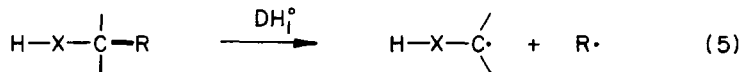
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Recent publications from our laboratory have demonstrated that [3,3]-sigma-tropic rearrangements (eq. 1) exhibit dramatic progressive rate acceleration, without any apparent change in mechanism, as the donor properties of the oxygen substituent are increased (M = H → M = K).[1,2] These observations have stimulated others to explore the possibility of promoting related [1,3]-sigmatropic processes (eq. 2).[3,4] Coincident with the above studies, Franzus[5] and Krow[6] have independ-ently reported examples of facile [1,3]-sigmatropic rearrangements which are strongly promoted by charged heteroatom substituents (eq. 3, eq. 4 respectively).
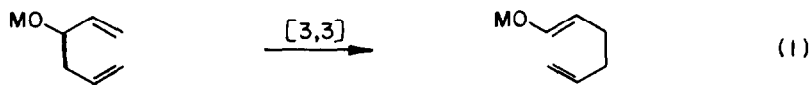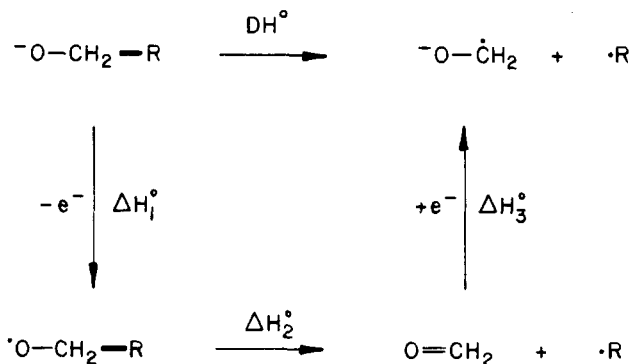

Similar to sigmatropic rearrangements in neutral molecules, rearrangements in charged systems may proceed <u>via</u> concerted or stepwise radical pathways.[7]

Unfortunately, no information is available on the perturbation of charged oxygen and nitrogen substituents on adjacent bond strengths (eq. 5, 6; X = O, N). We have thus attempted to estimate the gas phase bond dissociation energies DH_2° of

$$H-X-\overset{|}{\underset{|}{C}}-R \xrightarrow{DH_1^\circ} H-X-\overset{/}{\underset{\backslash}{C}}\cdot + R\cdot \qquad (5)$$

$$^-:X-\overset{|}{\underset{|}{C}}-R \xrightarrow{DH_2^\circ} {}^-:X-\overset{/}{\underset{\backslash}{C}}\cdot + R\cdot \qquad (6)$$

several alkoxides and to compare such values with the corresponding bond energy data DH_1° for alcohols. The resulting difference in bond energies is a measure of the substituent effect of O^-. Accordingly, we have established a simple Born-Haber cycle (Scheme I) which provides gas-phase bond dissociation energies DH_2° for primary alkoxide ions, R = H, CH_3, $CH_2CH=CH_2$.

Scheme I

$$^-O-CH_2-R \xrightarrow{DH^\circ} {}^-O-\dot{C}H_2 + \cdot R$$

$-e^- \Big| \Delta H_1^\circ \qquad\qquad\qquad +e^- \Big| \Delta H_3^\circ$

$$\cdot O-CH_2-R \xrightarrow{\Delta H_2^\circ} O=CH_2 + \cdot R$$

$$DH^\circ(\bar{O}CH_2-R) = EA(\dot{O}CH_2R) - EA(CH_2O) + DH^\circ(\dot{O}CH_2-R)$$

The limitation associated with this and related calculations is the availability of reliable gas phase thermochemical data for the illustrated processes. From the recent work of McIver and of Hamill, the gas phase electron affinities (EA) of simple alkoxy radicals are available, $\Delta H_1^\circ = EA(RO\cdot)$.[8,9] A few bond dissociation energies $DH^\circ(\cdot OCH_2-R)$ have either been determined or can be estimated.[10,12] Experimentally determined EA's for aliphatic carbonyl compounds, $\Delta H_3^\circ = -EA(RR'C=O)$, are generally unavailable. However, recent electron transmission spectroscopic studies on formaldehyde provide the most reliable measurement for its EA (-15.2 kcal/mol).[13] The calculated values for $DH^\circ(\bar{O}CH_2-R)$, literature values for $DH^\circ(HOCH_2-R)$,[10,14] and substituent effects are shown in Table I.

The data in Table I suggest that the effect of O^- in promoting bond homolysis is quite significant, ΔD = 13-17 kcal/mol. The origin of this observed bond weakening is differential stabilization of the radical by overlap with orbitals
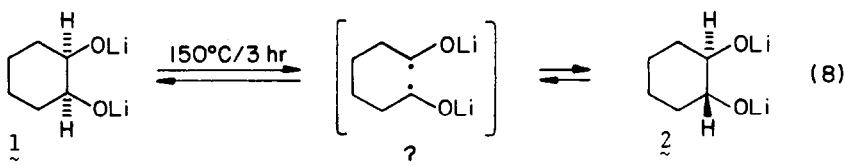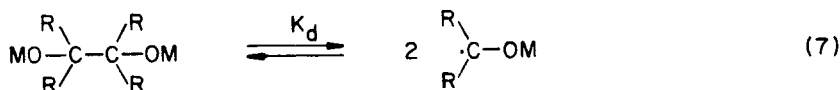
Table I.   Calculated Bond Dissociation Energies of $^-OCH_2$—R
and Substituent Effects for:[a]

$$XCH_2\text{—}R \longrightarrow XCH_2\cdot + \cdot R$$

R	$DH°(HOCH_2\text{—}R)$	$DH°(\bar{O}CH_2\text{—}R)$[b]	ΔD
H	93[c]	76	17
CH_3	83[c]	68	15
$CH_2CH{=}CH_2$	71[d]	58	13

[a]All values reported in kcal/mol.   [b]Gas phase, 298°K.   [c]Ref. 10.
[d]Ref. 14.

of the two oxygen species. Delocalization via a two-center three-electron bond
is better in $\cdot CH_2\text{-}O^-$ ($\cdot CH_2\text{-}O^- \longleftrightarrow CH_2\dot{=}O$) than in $\cdot CH_2OH$.[15] At this point one
can only speculate on the effects of counterions, M^+ (Li^+, Na^+, K^+), on
$DH°(MOCH_2\text{—}R)$. It is predicted, however, that electrostatic effects of M^+ will
cause a greater net stabilization of the charge-localized alkoxide than of the
charge-delocalized ketyl. These projections are consistent with the observation:
of Hirota on the counterion effects on pinacolate $\rightleftharpoons$ ketyl dissociation constant:
(eq. 7, R = fluorenyl).[16] Qualitatively, K_d increases with decreasing alkali
metal electronegativity (Li > Na > K). At the present time, no quantitative

$$MO\text{—}\underset{R}{\overset{R}{C}}\text{—}\underset{R}{\overset{R}{C}}\text{—}OM \quad \underset{\longleftarrow}{\overset{K_d}{\longrightarrow}} \quad 2 \; \underset{R}{\overset{R}{\cdot C}}\text{—}OM \qquad (7)$$

$$(8)$$

estimates can be made for the counterion effects on $DH°(MO\overset{|}{\underset{|}{C}}\text{—}R)$. Consequently,
reactions proceeding through proposed ketyl intermediates (eq. 8)[17] should be
critically re-examined to exclude other reasonable mechanisms.[18]
    Over the years there has accumulated a substantial body of data which
indicates that methoxide ion is an effective hydrogen atom donor (eq. 9).[19]
The data in Table I suggest that methoxide ion [$DH°(OCH_2\text{—}H)$ = 76 kcal/mol]
could be a better hydrogen atom donor than thiols [$DH°(CH_3S\text{-}H)$ = 88 kcal/mol[14]]
which are commonly employed hydrogen atom transfer substrates.

$$R\cdot \;+\; CH_3O^- \;\longrightarrow\; R{-}H \;+\; \cdot CH_2O^- \qquad (9)$$

The large magnitude of alkoxide substituent effects is in striking contrast to the initial intuitive prediction of many chemists that the effect would be small; however, the thermochemical values calculated above are consistent with recent experimental evidence.[1-5,19]

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