

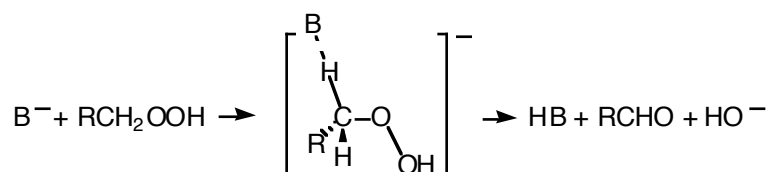
Gas Phase Reactions of Anions with Organic Hydroperoxides (ROOH)

Stephen J. Blanksby^a, Shuji Kato^b, G. Barney Ellison^b, Veronica M. Bierbaum^b^aDepartment of Chemistry, University of Wollongong, NSW, 2522, Australia^bDepartment of Chemistry and Biochemistry, University of Colorado, Boulder CO, 80309 USA

Organic hydroperoxides (ROOH) are one of the first oxidation products of lipids, proteins and DNA formed in living cells.¹ The subsequent reactions of these intermediates are extremely important in the biochemistry of oxidative stress. Despite their importance however, the reactions of peroxides have proven to be notoriously difficult to study due to the exceptional lability of the oxygen-oxygen bond ($DH_{298}[\text{RO-OH}] \approx 197 \text{ kJ mol}^{-1}$)² and the propensity of peroxides to be rapidly reduced by metal contaminants. These difficulties can be overcome by investigating the fundamental chemical reactivity of peroxides in the gas-phase where solvent and counter-ion interferences are completely absent. The gas phase reactions of organic peroxides with metal cations have been extensively studied by Schwarz and co-workers^{3,4} however little data is available concerning the reactions of anions with peroxides.

We have recently shown that alkyl hydroperoxides reacted with certain anions, in a flowing afterglow-selected ion flow tube (FA-SIFT), decompose to produce aldehydes and hydroxide ions (Scheme 1).⁵ Subsequent results indicate that this reactivity is general to strong and moderate gas phase bases such as $B = \text{HO}, \text{HCC}, \text{F}, \text{PhCC}$ but is not observed for weak gas phase bases such as $B = \text{NC}$ and Cl . Further, while this reaction proceeds efficiently for methyl and ethyl hydroperoxide, no reaction is observed for *tert*-butyl hydroperoxide. These data are consistent with a concerted elimination mechanism, which we have termed an $E_{\text{CO}2}$ reaction. Surprisingly, $B = \text{O}_2$ reacts efficiently with alkyl hydroperoxides to produce hydroxide anions despite its relatively weak gas phase basicity. This observation points to a possible electron transfer mechanism for the degradation of peroxides by radical anions. Experimental and computational results from these gas phase reactions will be discussed, along with the possible implications of these investigations for understanding biochemical pathways.

Scheme 1



References:

- (1) Halliwell, B.; Gutteridge, J. M. C. *Free radicals in biology and medicine*; 3rd ed.; Oxford University Press: Oxford, 1999.
- (2) Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2002**, *in press*.
- (3) Schalley, C. A.; Wesendrup, R.; Schroeder, D.; Weiske, T.; Schwarz, H. *J. Am. Chem. Soc.* **1995**, *117*, 7711-7718.
- (4) Schroeder, D.; Schalley, C. A.; Schwarz, H. In *DFG Report - Peroxide Chemistry*; Adam, W., Ed.; Wiley-VCH, 2000, pp 640-664.
- (5) Blanksby, S.; Ellison, G. B.; Bierbaum, V. M.; Kato, S. *J. Am. Chem. Soc.* **2002**, *124*, 3196-3197.