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Final Technical Report  
"Energy Partitioning in Elementary Chemical Reactions"  
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### Research Summary

The goals of this research are to measure the yields of all the important channels of the reactions of  $O(^3P)$  with unsaturated hydrocarbons and radicals. Also, we aim to measure product state distributions to understand the detailed mechanism of the reactive collisions.

We have studied the reactions of  $O(^3P)$  with terminal alkenes,  $RCH=CH_2$ , which produce vinyloxy radical,  $\bullet CH_2-CH=O$ . We use tunable laser excitation of vinyloxy to its electronically excited B state, which leads to bright fluorescence. By exciting the vinyloxy from excited vibrational levels in its ground electronic state to the vibrationless level of the B electronic state we probe the vibrational state distribution in it. This hot-band spectrum is very complex. It shows that the nascent vinyloxy is vibrationally excited in many different modes and combinations of modes. Characterization of the relaxation of these vibrationally excited levels help identify the vibrational quantum numbers associated with the hot bands in the spectrum. By studying reactions of a series of terminal alkenes we have determined that the R group acts as a bath that cools the vinyloxy product. This means the reaction complex must live long enough for internal vibrational redistribution to occur, that is, some tens of picoseconds.

We have studied the reaction of  $O(^3P)$  with isotopomers of propene to elaborate the reaction mechanism. We have used  $CH_3CH=CD_2$  ( $R=CH_3$ ) and find that products from attack at C-1 and C-2 appear in roughly equal amounts. This does not mean that reactions at C-1 and C-2 have the same probability. Attack at C-1 yields several different product channels. Attack at C-2 in contrast yields almost exclusively vinyloxy. Reaction of ethylene ( $R=H$ ), specifically its  $CH_2=CD_2$  isotopomer, produces a mixture of  $CH_2CDO$  and  $CD_2CHO$  with only small amount of  $CHDCDO$ . This shows that the channel of direct release of a hydrogen atom is preferred over the channel of indirect release via a hot acetaldehyde.

### Publications

B. Gherman, R. Friesner, T.-H. Wong, Z. Min, and R. Bersohn, *J. Chem. Phys.* **114**, 6128 (2001).

H. Su and R. Bersohn, *J. Chem. Phys.* **115**, 217 (2001).

H. Su and R. Bersohn, *J. Phys. Chem. A* **105**, 9178 (2001).

Chemical Physics, R. Bersohn and B. Berne, Chapter in *Encyclopedia of Science and Technology*, Vol. 2, Academic Press, New York, 2002.

R. Bersohn, *J. Chinese Chem. Soc.* **49**, 291 (2002).

H. Su and R. Bersohn, *J. Chem. Phys.* **117**, 8412 (2002).

M.J. Krisch, J.L. Miller, L.J. Butler, H. Su, R. Bersohn, and J. Shu, *J. Chem. Phys.* **119**, 176 (2003).

R. Bersohn, *Ann. Rev. Phys. Chem.* **54**, 1 (2003).