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Abstract



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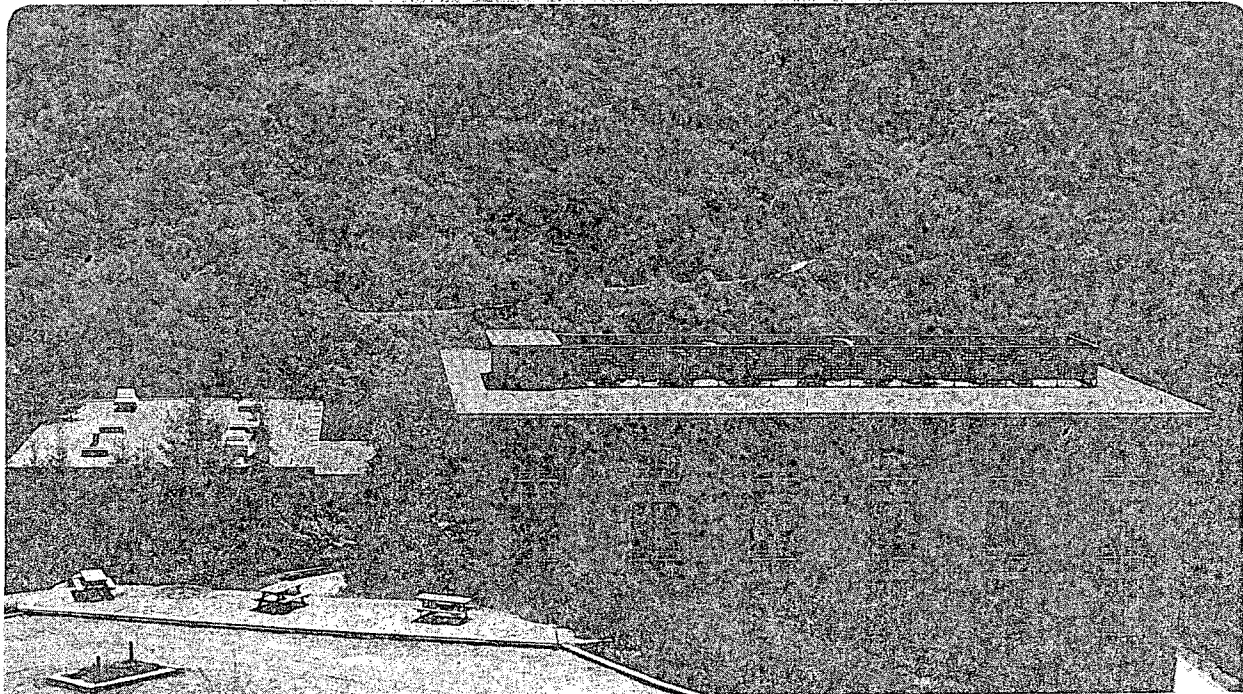
## Materials & Molecular Research Division

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REACTION MECHANISM OF OXYGEN ATOMS WITH UNSATURATED  
HYDROCARBONS BY THE CROSSED-MOLECULAR-BEAMS METHOD

Richard J. Buss, Robert J. Baseman, Guozhong He,  
and Yuan T. Lee

April 1982



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REACTION MECHANISM OF OXYGEN ATOMS WITH UNSATURATED  
HYDROCARBONS BY THE CROSSED-MOLECULAR-BEAMS METHOD

LBL--14321

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Richard J. Buss, Robert J. Baseman<sup>a</sup>, Guozhong He<sup>b</sup> and Yuan T. Lee<sup>c</sup>

Materials and Molecular Research Division, Lawrence Berkeley  
Laboratory and Department of Chemistry, University of California,  
Berkeley, California 94720 USA

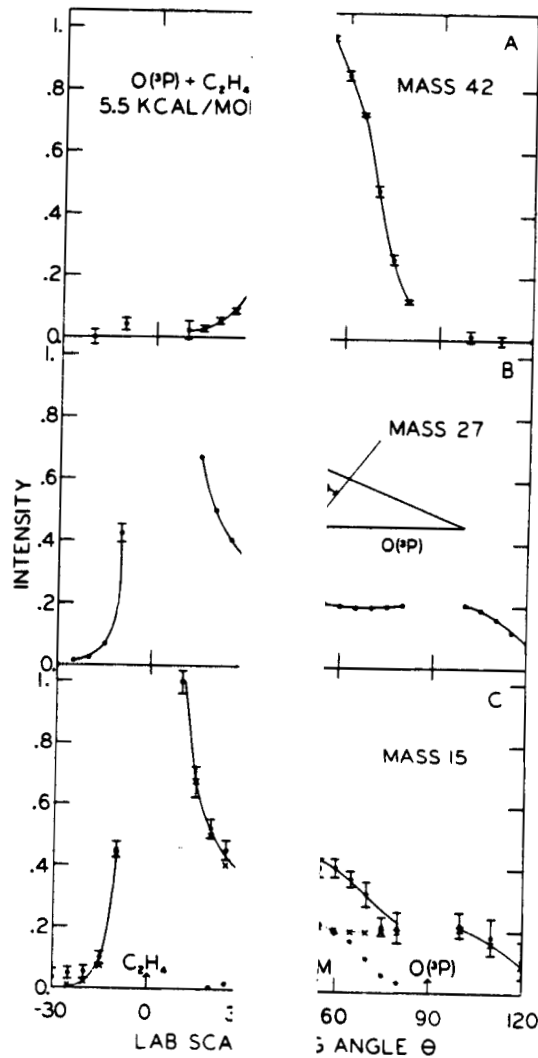
There are two basic experimental difficulties in the reaction of oxygen atoms with unsaturated hydrocarbons which prevented the elucidation of detailed reaction mechanism unambiguously. The first problem lies in the difficulty in the detection and identification of primary polyatomic radical products which are often highly energetic and do not give parent ions in the mass spectrometric detection. The second problem is associated with the fast secondary reactions initiated by primary products which makes it difficult to deduce primary products from the analysis of final products in the bulk experiments.

In our recent investigation of a series of reactions involving oxygen atoms with various unsaturated hydrocarbons including those containing halogen atoms, using the crossed molecular beams method, we have been able to overcome both these two problems and have determined the reaction mechanism unambiguously. Carrying out experiments under single collisions and observing primary products directly, the complication due to secondary reaction is avoided. By measuring the angular and velocity distributions of products at all the mass numbers which can be detected by the mass spectrometer, and from a comparison of these distributions, applying the requirement of energy and momentum conservation, primary products have been identified positively. For example, in the reaction  $O + C_2H_4$ , although major signals are detected at  $m/e = 15$  and  $29$ , they are found to be the daughter ions of  $CH_2CHO$  as shown in Fig. 1, rather than from  $CH_3$  and  $HCO$  as believed in many previous works.  $CH_2CHO$  is identified as the only major direct product under collision free conditions.

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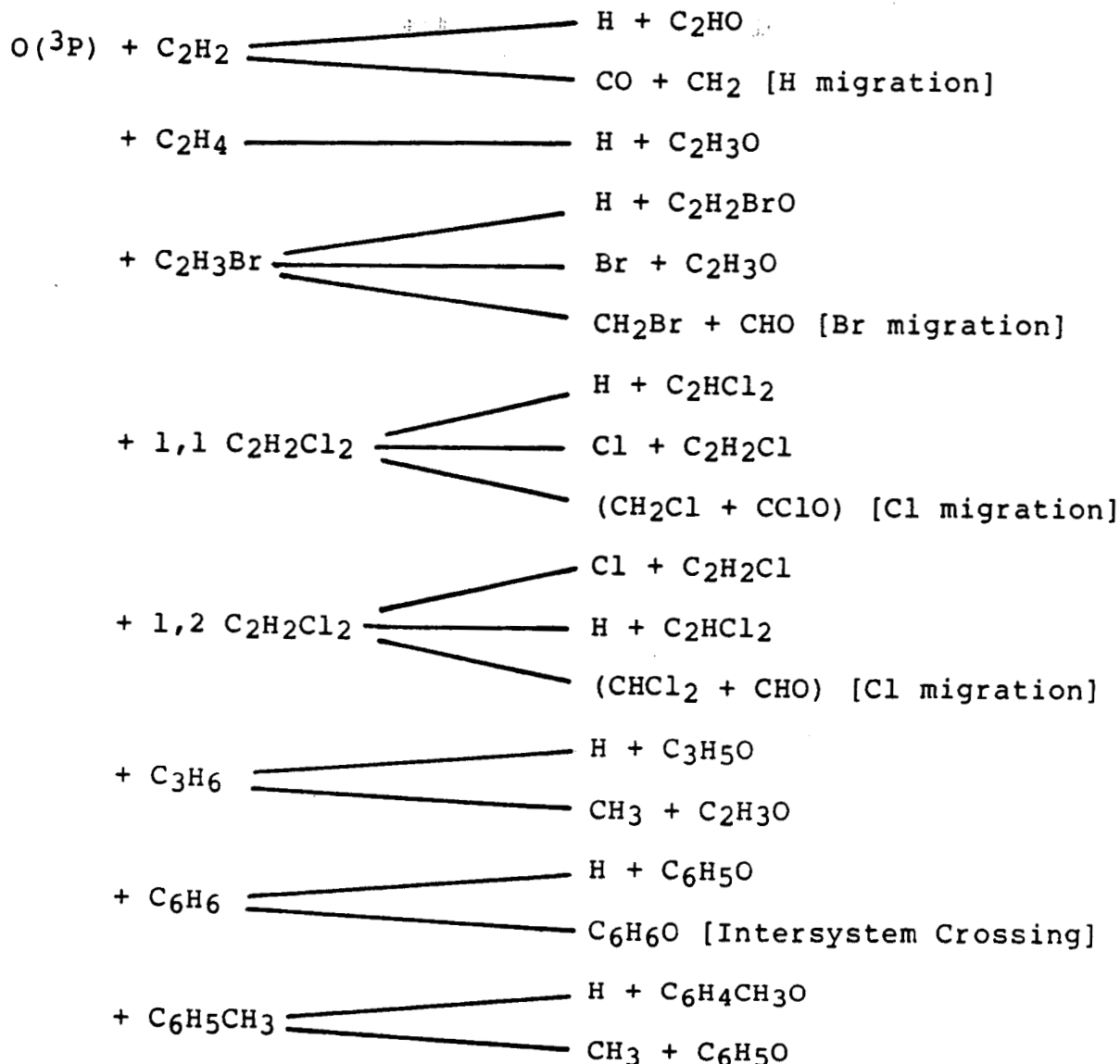
Fig. 1. Angular distributions of reaction products from the reaction  $O + C_2H_4$  at 5.5 kcal/mole collision energy. A.  $CH_2CHO$  product, B. Elastically scattered  $O(PP)$ , C. Mass 15 product. The intensity is arbitrary units.

Fig. 1. Angular distributions of reaction products from the reaction  $O + C_2H_4$  at 5.7 kcal/mole collision energy. A.  $CH_2CHO$  product, mass 27, C. Mass 15 product. The intensity is arbitrary units.

From a series of studies of the reaction of oxygen atoms with unsaturated hydrocarbons, it is found that the dominant reaction mechanism is substitution reactions with oxygen atoms replacing H, Cl, Br atoms or alkyl groups. The migration of H atom from one carbon to a neighboring carbon following the rupture of the original double bond was not found to be facile with acetylene, but the migration of H atom was found to be facile and to compete favorably with the simple substitution reactions.

The reaction of oxygen atoms with unsaturated hydrocarbons are summarized in Table 1, and are found to be the simple substitution reactions with oxygen atoms replacing H, Cl, Br atoms or alkyl groups. The migration of H atom from one carbon to a neighboring carbon following the rupture of the original double bond was not found to be facile, except in the reaction of Cl and Br atoms were found to be facile and to compete favorably with the simple substitution reactions.

Table 1. Primary Products of Reactions Between Oxygen Atoms with Unsaturated Hydrocarbons.



Some of the experimental findings, especially, the reaction mechanism of  $O(^3P) + C_2H_4$  have been substantiated by other experimental methods<sup>1-3</sup> and theoretical calculations.<sup>4</sup> In the quantum mechanical calculation of  $O(^3P) + C_2H_4$  interaction carried out by Dupuis et al.<sup>4</sup> it was, indeed, shown that the barrier from H atom migration is much higher than the barrier of the replacement of a H atom by an oxygen atom. In the reaction of  $O(^3P) + C_3H_6$ , the formation of  $H + C_3H_5O$  and  $CH_3 + C_2H_3O$  observed by Hunziker et al.<sup>3</sup> is also in agreement with our molecular beam investigations.

The experimental details of the mechanism of oxygen atom with unsaturated hydrocarbons by the crossed molecular beams method

This work was supported by the Office of Basic Energy Research, Office of Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract number DE-AC03-76SF00098.

The elucidation of reaction mechanism of oxygen atom with unsaturated hydrocarbons by the crossed molecular beams method will be discussed in detail.

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- b. Present address: Institut de Chimie Physique, Academie Sinica, Dalian, People's Republic of China.
- c. Miller Professor, 1981-1982
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