LBL-14321
Abstract

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

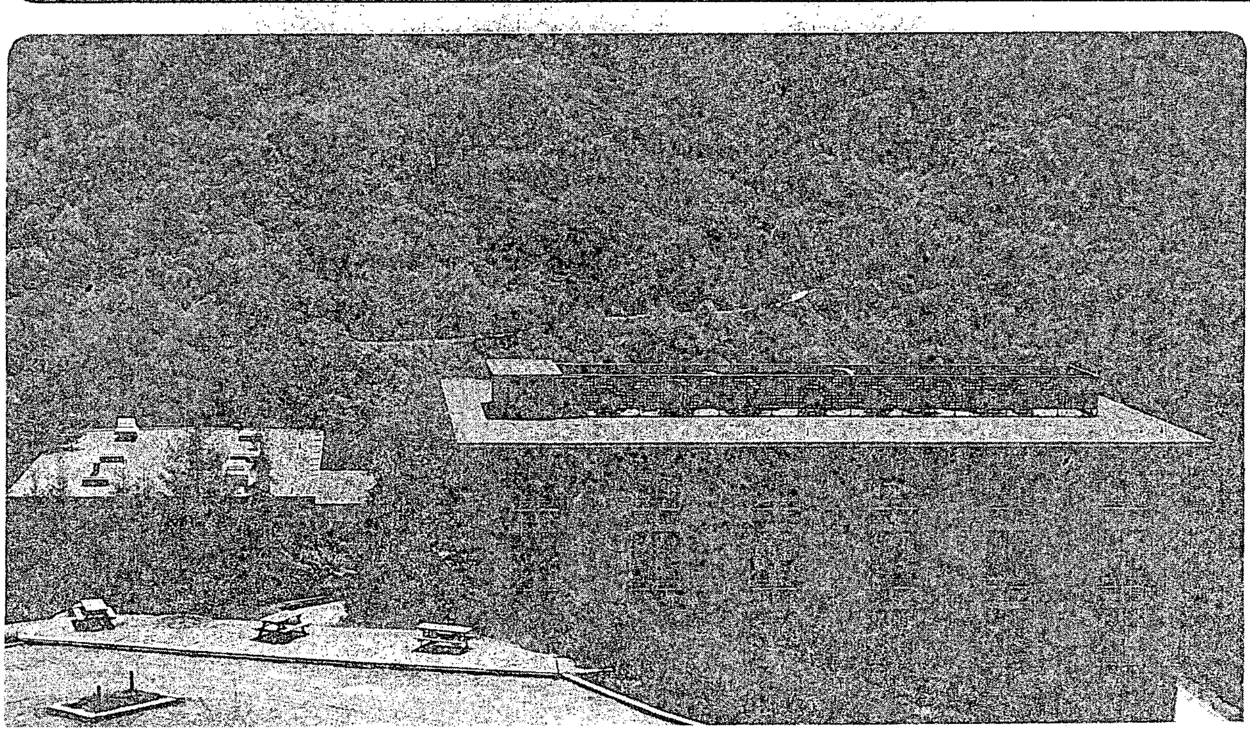
Materials & Molecular Research Division

To be presented at the International Symposium on Chemical Kinetics Related to Atmospheric Chemistry, National Institute for Environmental Studies, Ibaraki, Japan, June 6-10, 1982

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



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

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

LBL--14321

DE82 014994

Richard J. Buss, Robert J. Baseman[a], Guozhong He[b] and Yuan T. Lee[c]

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.

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

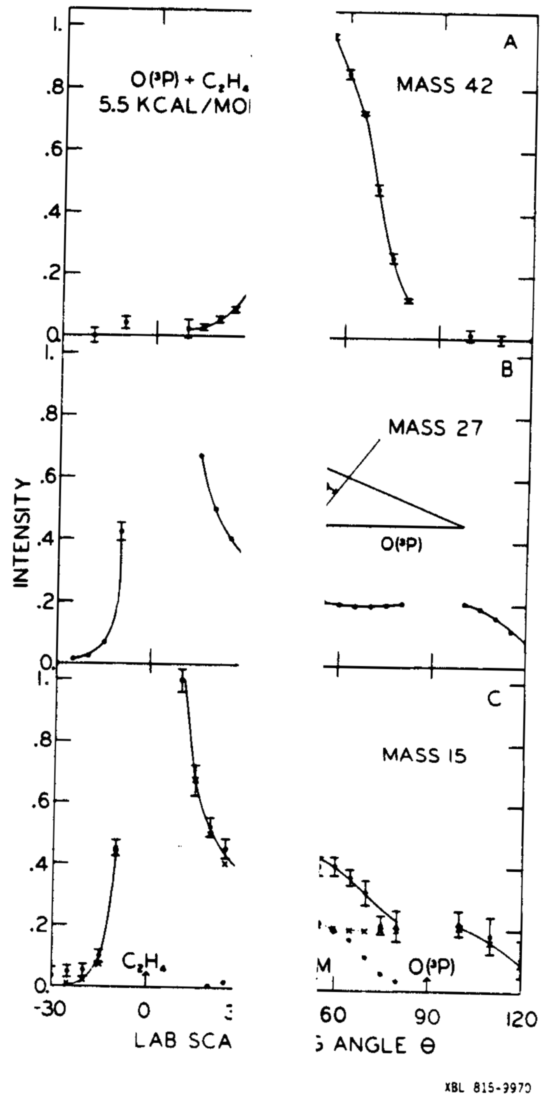


Fig. 1. Angular distribution: ... m the reaction O + C_2H_4 at 5.7 kcal/mole collision ... y. A. CH_2CHO product, B. Elastically scatt ... mass 27, C. Mass 15 subtraction of two c ... butions.

From a series of studies ... e reaction of oxygen atoms with unsaturated hydrocarbons ... are summarized in Table 1, the dominant reaction mechanis ... re found to be the simple substitution reactions with ox ... atoms replacing H, Cl, Br atom or alkyl groups. The mig ... n of H atom from one carbon to a neighboring carbon follow ... a rupture of the original double bond was not found to t ... place, except in the reaction with acetylene, but the migrat ... of Cl and Br atoms were found to be facile and to compete fa ... ly with the simple substitution reactions.

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

Reactants	Products
$O(^3P)$ + C_2H_2	H + C_2HO
	CO + CH_2 [H migration]
+ C_2H_4	H + C_2H_3O
+ C_2H_3Br	H + C_2H_2BrO
	Br + C_2H_3O
	CH_2Br + CHO [Br migration]
+ 1,1 $C_2H_2Cl_2$	H + C_2HCl_2
	Cl + C_2H_2Cl
	(CH_2Cl + CClO) [Cl migration]
+ 1,2 $C_2H_2Cl_2$	Cl + C_2H_2Cl
	H + C_2HCl_2
	($CHCl_2$ + CHO) [Cl migration]
+ C_3H_6	H + C_3H_5O
	CH_3 + C_2H_3O
+ C_6H_6	H + C_6H_5O
	C_6H_6O [Intersystem Crossing]
+ $C_6H_5CH_3$	H + $C_6H_4CH_3O$
	CH_3 + C_6H_5O

Some of the experimental findings, especially, the reaction mechanism of $O(^3P)$ + C_2H_4 have been substantiated by other experimental methods[1-3] and theoretical calculations.[4] In the quantum mechanical calculation of $O(^3P)$ + C_2H_4 interaction carried out by Dupuis et al.[4] 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.[3] is also in agreement with our molecular beam investigations.

The experimental details c .e elucidation of reaction mechanism of oxygen atom with u urated hydrocarbons by the crossed molecular beams method . be discussed in detail.

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

REFERENCES

a. John and Fannie Hertz Fell

b. Present address: Institut : Chemical Physics, Academia Sinica, Dalien, People's I ›lic of China.

c. Miller Professor, 1981-198

1. G. Inoue and H. Akimoto, J :em. Phys. 74, (1981) 425.

2. A. Luntz and K. Kleinermar ;. Phys. Chem. 85, (1981) 1966.

3. H. E. Hunziker, H. Kneppe H. R. Wendt, J. Photochem. 17, (1981) 389.

4. M. Dupuis, J. J. Wendolosk :. Takada and W. A. Lester, Jr., J. Chem. Phys. 76, (1 481.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720