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May 1983

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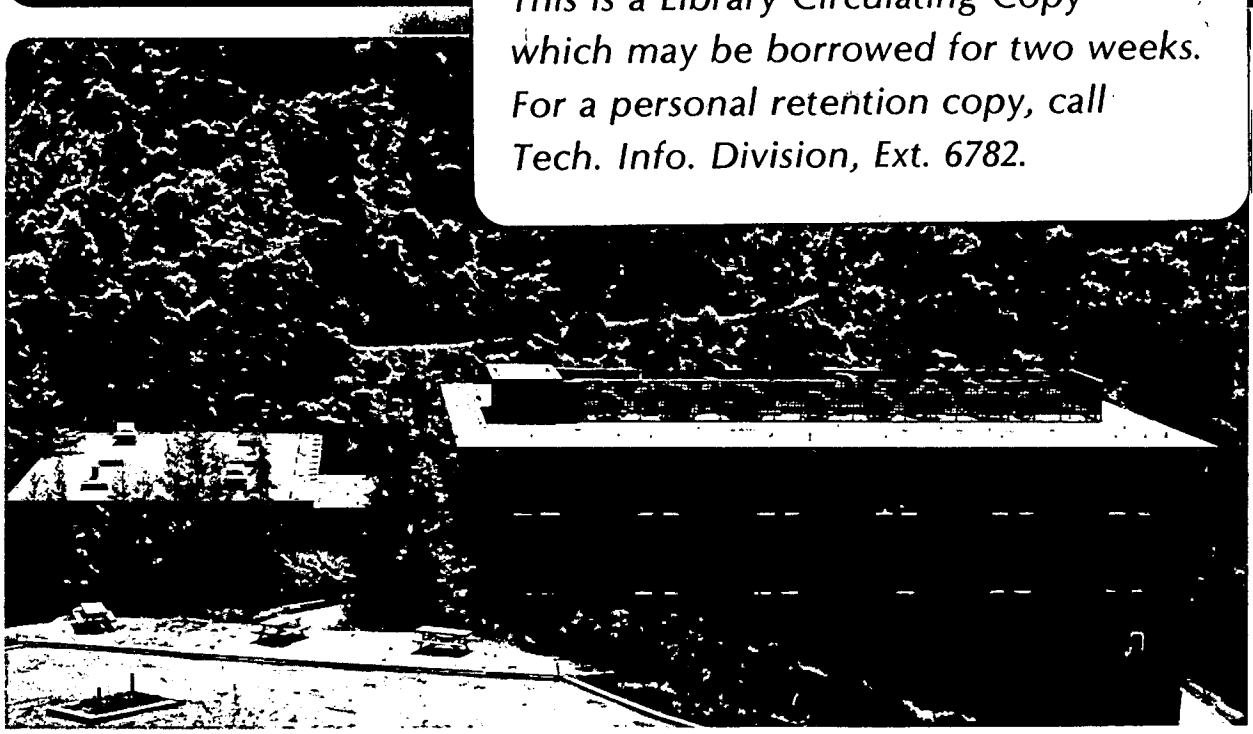

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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Theoretical Study of Oxidation Reactions: Mechanism of the $O(^3P) + H_2CO$ Reaction†

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In a continuing study of oxidation reactions, started with $O(^3P) + C_2H_4$ as a prototype for oxygen atom-olefin reactions,[1] we are presently investigating the mechanism of the reaction

$$O(^3P) + H_2CO \longrightarrow \text{products} \qquad (1)$$

important in the oxidation of methane, and thus of interest in combustion and in atmospheric chemistry.

It has long been assumed that the reaction of oxygen atoms with aldehydes proceeds through direct abstraction of the weak aldehydic hydrogen

$$O(^3P) + H_2CO \longrightarrow HCO + OH \ . \qquad (2)$$

Recently, Chang and Barker[2] reported the measurement of a substantial yield (~ 30%) of a primary product of mass 44, suggesting that the addition reaction is an important channel,

$$O(^3P) + H_2CO \longrightarrow H_2COO(^3B_2) \ . \qquad (3)$$

The H_2COO adduct would then undergo isomerization followed by fragmentation,

$$H_2COO(^3B_2) \longrightarrow HCOOH(^3A_1) \qquad (4)$$

$$HCOOH(^3A_1) \longrightarrow H + HOCO \qquad (5.a)$$

$$\longrightarrow H + HCOO \qquad (5.b)$$

$$\longrightarrow HCO + OH \qquad (5.c)$$

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†Work 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 No. DE-AC03-76SF00098.

Experiments by Kleinermanns and Luntz[3] indicated that hydroxyl radical formation in (1) is the result of a single collision event in accord with reaction (2). These authors concluded that the addition reaction (3) is not important for the formation of OH under molecular beam condition.

We have initiated an ab initio MCHF/CI study of the elementary steps (2)-(4). To date the following results have been obtained:

i) the transition state structure for the abstraction reaction (2) corresponds essentially to collinear attack of the oxygen atom on one of the CH bonds.

ii) the energy barrier for hydrogen migration is large (~ 50 kcal/mole) as shown in Fig. 1. The calculated relative energies (experimental values in parentheses) are given in Table 1. The energy of $O(^3P) + OCH_2$ relative to H_2COO obtained from thermochemical data is shown in Fig. 1. These results imply that in a room temperature molecular beam experiment, the isomerization of $H_2COO(^3B_2)$ by hydrogen migration is not an accessible channel. This conclusion supports Kleinermanns and Luntz's experimental finding that the OH product does not originate from a reaction intermediate as in reaction (5.c).

Present efforts are directed toward obtaining accurate energy barriers for the abstraction reaction (2) and the addition reaction (3). Furthermore, hydrogen elimination

$$H_2COO(^3B_2) \longrightarrow H + HCO_2 \qquad (6)$$

is being explored as a possible channel for fragmentation of the adduct H_2COO analogous to vinoxy radical formation, i.e.,

$$CH_2\text{-}CH_2\text{-}O \longrightarrow H + CH_2CHO \qquad (7)$$

in the $O(^3P) + C_2H_4$ reaction.

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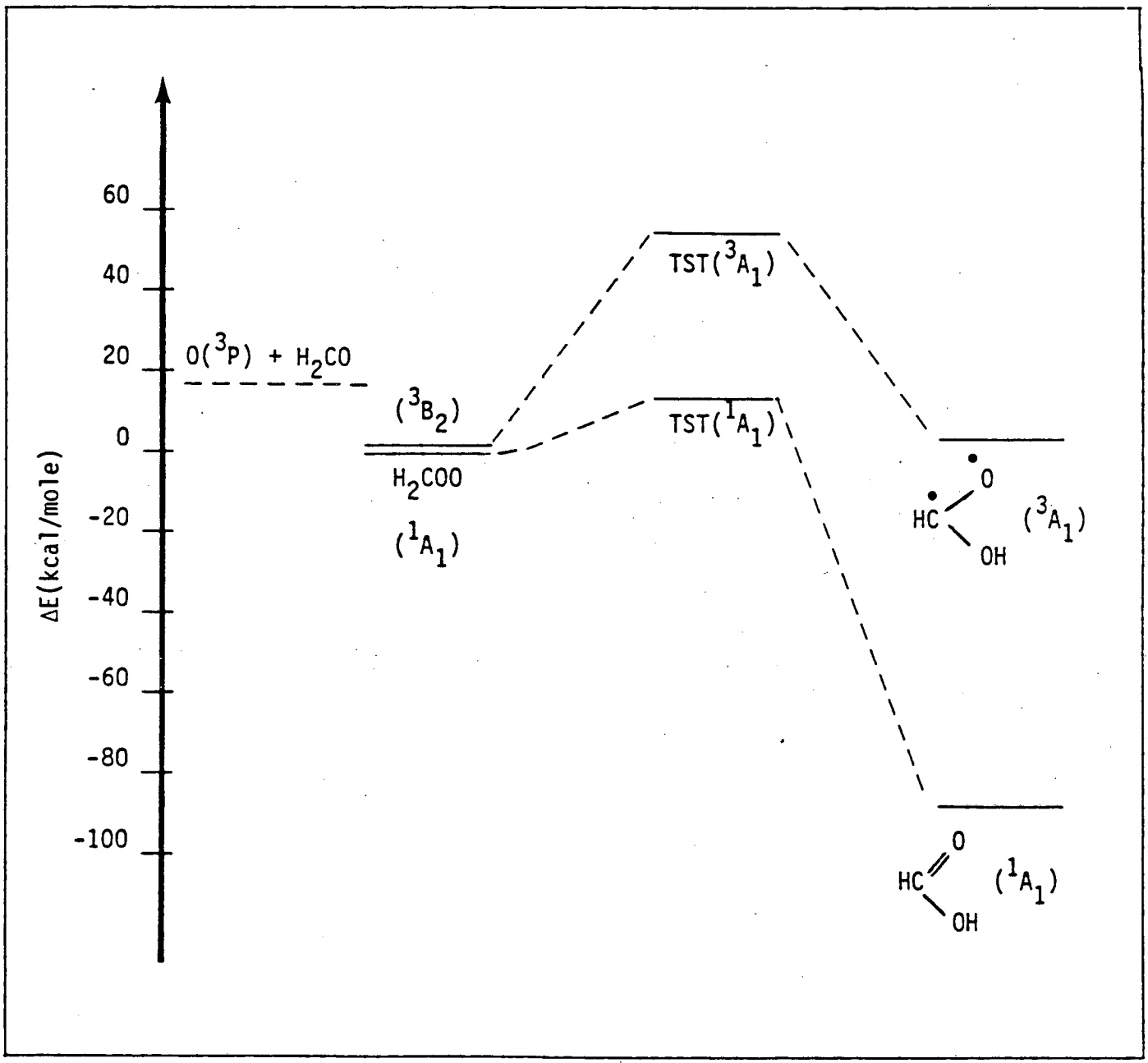
Table I Relative Energies (Kcal/mole) for the Hydrogen Migration Reaction $H_2COO \rightarrow HCOOH$

	H_2COO	TST	HCOOH
Singlet	0	+13	-87(-110)
Triplet	1	+53	+5(-9)

Fig. 1 Hydrogen Migration Reaction $H_2COO \rightarrow HCOOH$



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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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