# Exploring the Dynamics of Reactions of Oxygen Atoms in States $^3$P and $^1$D with Ethene at Collision Energy 3 kcal mol$^{-1}$

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The reaction of atomic oxygen with ethene ($C_2H_4$) plays an important role in the combustion of ethene and other hydrocarbon fuels because ethene might be an intermediate in the combustion of most hydrocarbons. Numerous experimental and theoretical efforts have been devoted to investigations of the reaction of $^3$P O atoms with $C_2H_4$. Shown below are some likely product channels for the reaction O + $C_2H_4$.

$$O + C_2H_4 \rightarrow CH_2CHO + H \quad (1)$$
$$\rightarrow CH_3CO + H \quad (2)$$
$$\rightarrow CH_2CO + H_2 \quad (3)$$
$$\rightarrow CH_3 + HCO \quad (4)$$
$$\rightarrow CH_2(\tilde{X}\,^3B_1) + HCHO \quad (5)$$
$$\rightarrow CH_2(\tilde{a}\,^1A_1) + HCHO \quad (6)$$
$$\rightarrow CH_4 + CO \quad (7)$$
$$\rightarrow CH_2CO + 2H \quad (8)$$

The enthalpies $\Delta H^o_{0K}$ of reactions (1) – (8) for $^3$P O reactants were computed to be -17.0, -23.5, -85.1 (-84.2), -28.8 (-27.9), -6.6 (-5.4), 2.3 (3.6), –116.7 (–117.4), and 18.5 (19.0) kcal mol$^{-1}$, respectively; the numbers within parentheses are experimental values. For O $^1$D reactant, the $\Delta H^o_{0K}$ values are 45.4 kcal mol$^{-1}$ less than for O $^3$P reactant.

A source chamber equipped with a solenoid valve (Even-Lavie) and a discharge device served to generate a sequence of pulses of oxygen atoms. Two gaseous mixtures – 20% $O_2$ + 80% He (mixture 1) and 3% $O_2$ + 12.5% Ar + 84.5% He (mixture 2) – served as discharge media. The Even-Lavie valve expanded a gaseous mixture at a stagnation pressure 104 psi. A discharge device with two electrodes and several insulators was installed on the outlet plate of the valve; electrodes and insulators have orifices (diameter 1–2 mm) at the center for gas penetration. A dc power supply, an RC circuit, and two rapid high-voltage switches together served to constrain the discharge to a pulse of width 10 μs. Discharges occurred while gas pulses passed through the discharge region. Gaseous mixtures 1 and 2 generated oxygen atoms in states $^1$D and $^3$P with a population ratio 0.17 % and 3.5 %, respectively. In the other source chamber, a molecular beam of ethene was generated with another Even-Lavie valve that expanded neat ethene at a backing pressure 54 psi and 110 $^o$C. The velocities of atomic oxygen and ethene were evaluated to be 1285 m s$^{-1}$ and 880 m s$^{-1}$, respectively, which produced $E_c$ = 3 kcal mol$^{-1}$ for the reaction O + $C_2H_4$.

The left panels of Fig. 1 show TOF spectra of species with *m*/*z* = 15 recorded at selected particular laboratory angles from –18$^o$ to 108$^o$ using mixture 1 as the discharge medium. The TOF spectra for *m*/*z* = 15 recorded near $\Theta_{CM}$ exhibit three features; the rapid (first) feature is assigned to product $CH_3$ from reaction (4a), and the two slow (second and third) features to daughter ions of product $CH_2CHO$ from reaction (1a); the second and third features correspond to the $CH_2CHO$ products scattered forward and backward, respectively, to the detector in the CM frame. The two slow features became unimodal and small as the laboratory angle increases/decreases from $\Theta_{CM}$. Product $CH_3$ with a large velocity is observable from –18$^o$ to 108$^o$. With mixture 2 as the discharge medium, an additional component peaking at ~ 55 μs appears in each TOF spectrum at *m*/*z* = 15 as shown in the right panels of Fig. 1; this component is assigned to product $CH_3$ from Reaction (4b).

With a simulation program we mimicked the angle-specific TOF spectra of a product with trial kinetic-energy distributions $P(E_t; \theta)$ ($\equiv d^2\sigma/dE_t d(\cos\theta)$) at every 30$^o$ and a trial angular distribution $P(\theta)$ ($\equiv d\sigma/d(\cos\theta)$) based on an algorithm of forward convolution. A kinetic-energy distribution at an arbitrary angle is derivable by interpolation. $E_t$ is the total kinetic energy of two momentum-matched products; θ is the angle of a product scattered with respect to the relative velocity of reactant atomic oxygen in the CM frame. From the best fits to all TOF spectra in Fig. 1, we derived distributions of $P(E_t; \theta)$ and $P(\theta)$ for reactions (1a), (4a) and (4b). The reactivity of O $^1$D with ethene is ca. 90 times that of O $^3$P for the channel to eliminate $CH_3$.

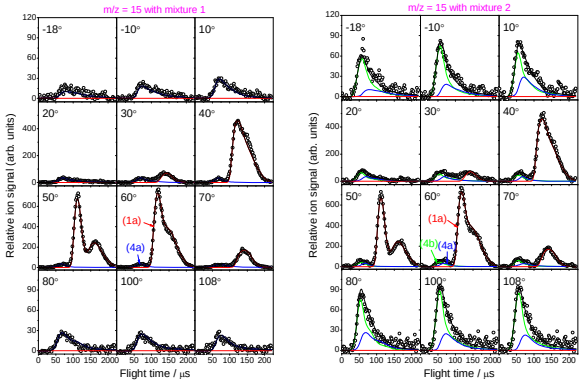


**Fig. 1:** Angle-specific TOF spectra of products $CH_2CHO$ and $CH_3$ recorded at *m*/*z* = 15 with photoionization energy 12.8 eV. Mixtures 1 and 2 served as the discharge medium. Red and blue lines denote the mimicked TOF spectra of product $CH_2CHO$ from Reaction (1a) and of product $CH_3$ from Reaction (4a), respectively. A thin black line represents the sum of spectra depicted with red and blue lines. The yield of product $CH_3$ from Reaction (4b) is negligibly small. Each panel shows the corresponding laboratory angle Θ. Each TOF spectrum was accumulated for 3 ×10$^5$ trigger pulses.