

# Reaction of O(<sup>3</sup>P) with C<sub>2</sub>H<sub>4</sub>: Yield of the Reaction Products as a Function of Temperature.

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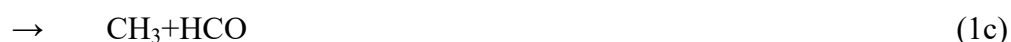
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## ABSTRACT

Reaction of oxygen atoms with ethylene is an important step in combustion process particularly affecting the profiles of intermediate species and flame speed. Currently, the relative importance of different pathways of this multichannel reaction at different temperatures is not fully established and determination of the branching ratios for different reaction channels as a function of temperature remains essential for modeling combustion systems. In the present work, the products of  $O(^3P)+C_2H_4$  reaction have been studied over an extended temperature range (297 – 900 K) using a low pressure flow reactor (1–8 Torr) combined with a quadrupole mass spectrometer. The yields of the three main reaction products, H-atom,  $CH_3$  radical and  $CH_2O$ , were determined to be  $0.31 \pm 0.05$ ,  $0.53 \pm 0.09$  and  $0.17 \pm 0.03$ , respectively, independent of pressure and temperature under experimental conditions of the study. For the yields of the minor reaction products,  $H_2$  and  $CH_4$ , the upper limits were determined as 0.05 and 0.02, respectively. These results are compared with the experimental data and theoretical calculations available in the literature.

## 1. INTRODUCTION

Ethylene is one of the key species of the kinetic mechanisms in combustion chemistry being an important intermediate in the oxidation of methane and larger hydrocarbons.<sup>1</sup> Once formed, C<sub>2</sub>H<sub>4</sub> can react with atoms or radicals (mainly OH, O, HO<sub>2</sub>). Reaction with oxygen atoms is one of the dominant degradation pathways of the alkenes and is an important step in combustion processes particularly affecting the profiles of intermediate species and flame speed. In addition to its importance in combustion, the reaction of ethylene with triplet oxygen is of great fundamental interest with regard to a complex mechanism with a variety of competitive reaction pathways:<sup>2-3</sup>

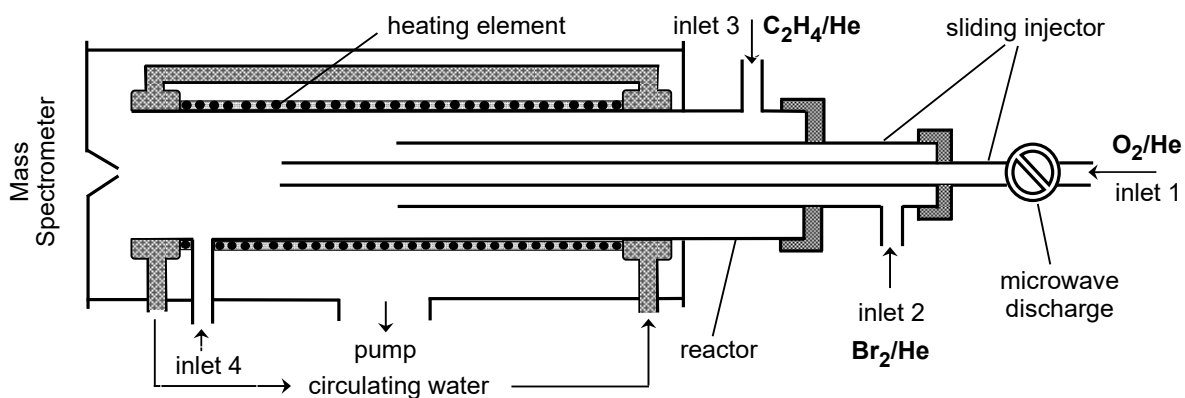


The theoretical and practical interests to reaction of O-atom with ethylene initiated an extensive research, experimental and theoretical, of this reactive system over the past few decades (refs. 2-4 and references therein). Currently, the total reaction rate constant can be considered as well known over a wide temperature range extending from atmospheric temperatures to those in combustion.<sup>4</sup> As for the mechanism of this multichannel reaction, the relative importance of different reaction pathways at different temperatures has not yet been fully established. Determination of the primary reaction products and branching ratios for different reaction channels as a function of temperature remains essential for modeling combustion systems.

In this work, we report the results of a first systematic study of the branching ratios for all the reactive channels of reaction (1) as a function of temperature in the range  $T = 297 - 900\text{K}$ .

## 2. EXPERIMENTAL

Experiments were carried out in a discharge flow reactor using a modulated molecular beam electron impact ionization (with ion source operating at 25-30 eV) mass spectrometer as the detection method. The flow reactor consisted of an electrically heated Quartz tube (45 cm length and 2.5 cm i.d.) with water-cooled extremities (Figure 1).<sup>5</sup> Temperature in the reactor ( $T = 297 - 900\text{K}$ ) was measured with a *K*-type thermocouple positioned in the middle of the reactor in contact with its outer surface. Temperature gradients along the flow tube measured with a thermocouple inserted in the reactor through the movable injector was found to be less than 1%.<sup>5</sup>



**Figure 1.** Diagram of the flow reactor.

The experimental approach used in the measurements of the yields of the products of reaction (1) consisted in titration of oxygen atoms with a mixture of  $\text{C}_2\text{H}_4$  and  $\text{Br}_2$ . Similar approach, however with addition of  $\text{Cl}_2$  into  $\text{O} + \text{C}_2\text{H}_4$  reactive system, was employed previously by Peeters & Maes.<sup>6</sup> The presence of relatively high concentration of  $\text{Br}_2$  in the

reactor ( $[\text{Br}_2] = (2 - 8) \times 10^{13}$  molecule  $\text{cm}^{-3}$ ) allows (i) to transform the labile products of reaction (1) into the stable species which can be easily and in an absolute way recorded with mass spectrometer and (ii) to avoid the very rapid secondary reactions of the radicals formed in reaction (1) with oxygen atoms. In this way, in addition to formaldehyde (channel 1d) which was detected directly at its parent peak ( $m/z = 30$ ,  $\text{CH}_2\text{O}^+$ ), we were able to detect two other main products of reaction (1), H (channels 1a and 1b) and  $\text{CH}_3$  (channel 1c) at  $m/z = 80/82$  ( $\text{HBr}^+$ ) and  $94/96$  ( $\text{CH}_3\text{Br}^+$ ), respectively:



$$k_2 = 6.7 \times 10^{-10} \exp(-680/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (T = 214-295\text{K})^7$$



$$k_3 = 2.0 \times 10^{-11} \exp(197/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (T = 296-532\text{K})^8$$

Although no reliable rate constant data are available for reactions (2) at high temperatures, it is obvious that under experimental conditions of the present study ( $[\text{Br}_2] = (2 - 8) \times 10^{13}$  molecule  $\text{cm}^{-3}$ , reaction time in temperature controlled zone = (3 – 5) ms, flow rates being in the range 1450- 2500  $\text{cm s}^{-1}$ ) the reaction is fast enough to rapidly scavenge hydrogen atoms in the whole temperature range of the study.

Oxygen atoms generated from the microwave discharge in  $\text{O}_2/\text{He}$  mixtures were introduced into the reactor through the inner tube of the movable injector (Figure 1). In presence of only  $\text{Br}_2$  in the reactor, the oxygen atoms are totally transformed to  $\text{BrO}$  (reaction 4) detected at  $m/z=95/97$  as  $\text{BrO}^+$  and corresponding to initial concentration of O-atoms:



Surprisingly, the rate constant of the reaction (4) (widely used as a source of  $\text{BrO}$  radicals in laboratory studies) is not well established: it is in the range  $(1.4 - 2) \times 10^{-11}$   $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at room temperature and has a negative temperature dependence.<sup>9-10</sup> The concentration of O consumed in reaction with  $\text{C}_2\text{H}_4$ ,



$$k_1 = 2.25 \times 10^{-17} T^{1.88} \exp(-92/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (T = 220 - 2000 \text{ K}),^4$$

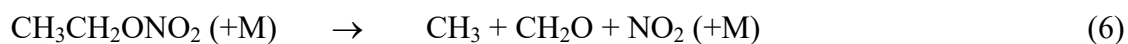
was determined as a difference between initial concentration of BrO (recorded in the absence of C<sub>2</sub>H<sub>4</sub> in the reactor) and concentration of BrO recorded in the presence of both Br<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> in the reactor.

Absolute calibration of BrO signals was realized by chemical conversion of BrO to NO<sub>2</sub> through reaction (5) conducted in excess of NO (flowed through inlet 4) with subsequent detection of NO<sub>2</sub> formed ([BrO]<sub>0</sub> = [NO<sub>2</sub>]<sub>formed</sub>):



$$k_5 = 8.7 \times 10^{-12} \exp(260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over } T = 220\text{-}430\text{K}.^{11}$$

The absolute concentrations of NO<sub>2</sub> as well as of other stable species (Br<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>Br, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>ONO<sub>2</sub>) in the reactor were calculated from their flow rates obtained from the measurements of the pressure drop of their mixtures in He stored in calibrated volume flasks. Absolute concentration of HBr was determined using reaction (2) in excess of Br<sub>2</sub>. In this case, H-atoms produced in microwave discharge of H<sub>2</sub>/He mixtures were titrated with Br<sub>2</sub> and concentration of HBr was determined from the consumed fraction of Br<sub>2</sub>, [HBr] = Δ[Br<sub>2</sub>]. The absolute calibration of the mass spectrometer for formaldehyde was realized by injecting known amounts (0.2–0.8 μL) of the 36.5 % wt solution of CH<sub>2</sub>O in water inside the flow tube, and recording the parent mass peak intensity of CH<sub>2</sub>O at m/z = 30. The integrated area of the mass spectrometric signals corresponding to known total number of CH<sub>2</sub>O molecules injected into the reactor allowed the determination of the calibration factor. Another alternative method used for absolute calibrations of CH<sub>2</sub>O and CH<sub>3</sub>Br consisted in thermal decomposition of ethyl nitrate (at T ≥ 500K) in presence of Br<sub>2</sub> in the reactor:

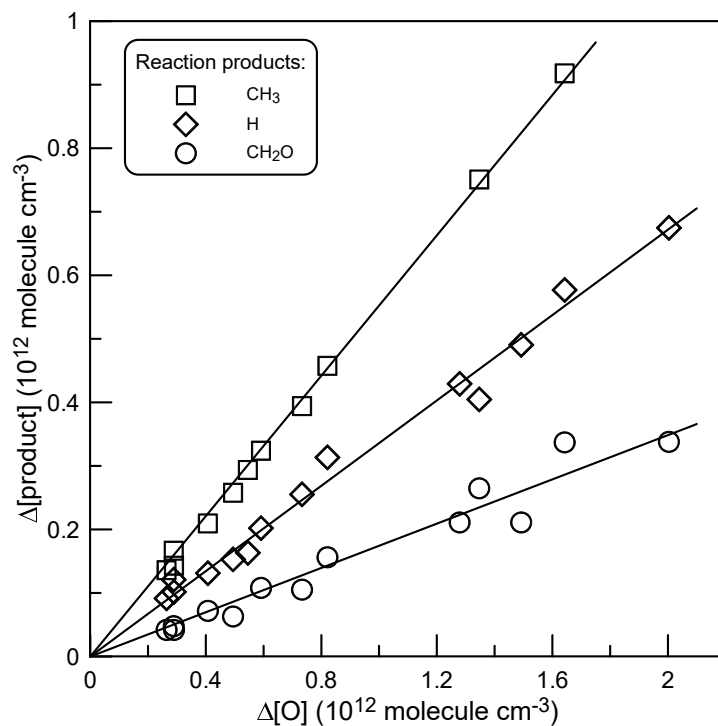


(products of this reaction were studied in an unpublished work from our group). Experimentally, total consumption of the nitrate and appearance of the decomposition products,  $\text{NO}_2$ ,  $\text{CH}_2\text{O}$  and  $\text{CH}_3$  (converted to  $\text{CH}_3\text{Br}$  in presence of  $\text{Br}_2$ ) was observed and absolute concentrations of the species could be determined in accordance with:  $[\text{CH}_3\text{Br}] = [\text{CH}_2\text{O}] = [\text{NO}_2] = [\text{C}_2\text{H}_5\text{ONO}_2]_0$ . The results of this calibration method were in good agreement (within 10-15%) with that by injection of  $\text{CH}_2\text{O}$  and measurements of  $[\text{CH}_3\text{Br}]$  and  $[\text{NO}_2]$  from their calibrated mixtures.

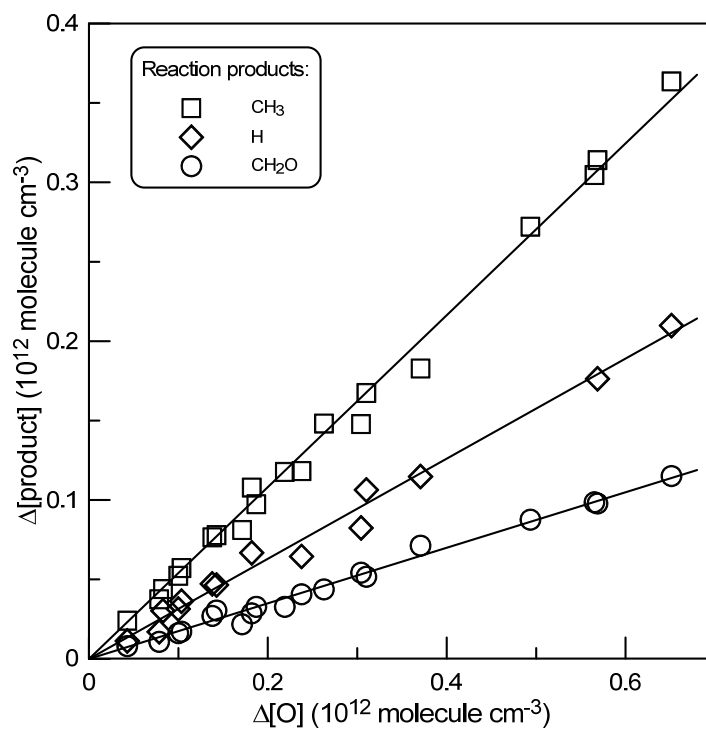
Ethyl nitrate was synthesized in the laboratory through reaction of ethanol with  $\text{H}_2\text{SO}_4:\text{HNO}_3$  (1:1) mixture.<sup>12</sup> Gas chromatographic analysis of  $\text{C}_2\text{H}_5\text{ONO}_2$  has shown that impurities were less than 0.1%. The purities and origin of other gases used were as follows: He >99.9995% (Alphagaz), was passed through liquid nitrogen traps;  $\text{O}_2$  > 99.995% (Alphagaz);  $\text{H}_2$  > 99.998% (Alphagaz);  $\text{C}_2\text{H}_4$  >99.99% (Phillips);  $\text{Br}_2$  >99.99% (Aldrich);  $\text{CH}_3\text{Br}$  > 99% (Aldrich);  $\text{NO}_2$  > 99% (Alphagaz);  $\text{NO}$  > 99% (Alphagaz);  $\text{CH}_2\text{O}$ , 36.5 wt. % in  $\text{H}_2\text{O}$  (Sigma-Aldrich).

### 3. RESULTS AND DISCUSSION

**3.1. Yield of the reaction products.** Experiments consisted in the measurements of the concentration of oxygen atoms consumed in reaction with  $\text{C}_2\text{H}_4$  and those of three main reaction products formed: H atoms (detected as HBr),  $\text{CH}_3$  radicals (detected as  $\text{CH}_3\text{Br}$ ) and  $\text{CH}_2\text{O}$ . The measurements were carried out at 1 Torr total pressure of helium and temperature in the range 297 – 900 K. Experimental conditions are presented in Table 1. The results of the measurements are shown in Figures 2 and 3 (and Figures S1 – S3 of Supporting information (SI)).

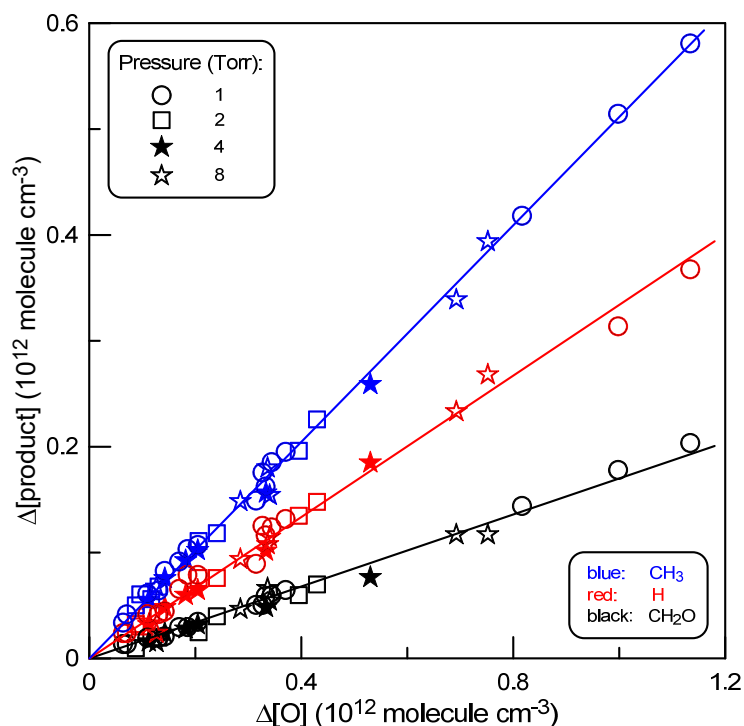


**Figure 2.** Concentration of products of reaction (1) as a function of consumed concentration of oxygen atoms:  $T = 297\text{K}$ ,  $P = 1$  Torr.



**Figure 3.** Concentration of products of reaction (1) as a function of consumed concentration of oxygen atoms:  $T = 614\text{K}$ ,  $P = 1$  Torr.





**Figure 4.** Concentration of products of reaction (1) as a function of consumed concentration of oxygen atoms measured at different pressures in the reactor:  $T = 900\text{K}$ ,  $P = (1 - 8)$  Torr.

At  $T = 900$  K the yield of the reaction products was measured as a function of pressure between 1 and 8 Torr of He. Results of the measurements are presented in Figure 4. One can note that in the pressure range of the present study the yields of the reaction products are independent of pressure. All the results obtained for the yields of H, CH<sub>3</sub> and CH<sub>2</sub>O (determined as slopes of the linear through origin fits to the experimental data in Figures 2-4 and S1-S3 of SI) are shown in Table 1.

**Table 1. Summary of Experimental Conditions and Results of the Measurements of the Yields of CH<sub>3</sub>, H and CH<sub>2</sub>O in Reaction O+C<sub>2</sub>H<sub>4</sub>.**

| $T, \text{K}$ | $^a[\text{O}]_0 \times 10^{-12}$ | $^a[\text{C}_2\text{H}_4] \times 10^{-15}$ | $[\text{C}_2\text{H}_4]/[\text{Br}_2]$ | $^b$ yields of the reaction products |       |                   |
|---------------|----------------------------------|--|--|--------------------------------------|-------|-------------------|
|               |                                  |  |  | CH <sub>3</sub>                      | H     | CH <sub>2</sub> O |
| 297           | 0.41-2.70                        | 0.19-2.15                                  | 4.1-39.5                               | 0.552                                | 0.336 | 0.174             |
| 365           | 0.46-2.90                        | 0.13-0.89                                  | 1.7-21.2                               | 0.528                                | 0.283 | 0.173             |
| 450           | 0.32-2.04                        | 0.12-0.64                                  | 3.5-23.0                               | 0.550                                | 0.300 | 0.152             |
| 614           | 0.20-1.40                        | 0.02-0.44                                  | 1.6-12.3                               | 0.541                                | 0.315 | 0.175             |
| 730           | 0.29-1.50                        | 0.04-0.27                                  | 1.0-6.6                                | 0.527                                | 0.300 | 0.176             |
| 900           | 0.16-1.40                        | 0.03-0.32                                  | 1.4-8.9                                | 0.511                                | 0.329 | 0.177             |

<sup>a</sup> units are molecule cm<sup>-3</sup>

<sup>b</sup> estimated uncertainty on the yields of the reaction products is (15-20)%.

The measured yields of the products of reaction (1) can be considered as independent of temperature and the following mean values can be recommended from the present study in the temperature range  $T = 297\text{-}900\text{K}$ :

$$(k_{1a} + k_{1b})/k_1 = 0.31 \pm 0.05$$

$$k_{1c}/k_1 = 0.53 \pm 0.09$$

$$k_{1d}/k_1 = 0.17 \pm 0.03$$

The quoted nearly 15-20% combined uncertainty of the measurements includes statistical error (within a few percent) and those on the measurements of the absolute concentrations of BrO (10%) and reaction products (10-15%). Let's note that the sum of the branching ratios for the CH<sub>3</sub>, H and CH<sub>2</sub>O forming pathways of reaction (1) is nearly 1.

The branching ratios for the minor channels (1e) and (1f) were explored in separate experiments carried out at  $T = 900\text{ K}$  and 1 Torr total pressure. The corresponding targeted products were H<sub>2</sub> and CH<sub>4</sub>. For the concentration of oxygen atoms of  $2.3 \times 10^{12}$  molecule cm<sup>-3</sup> consumed in reaction with C<sub>2</sub>H<sub>4</sub>, the concentrations of formed H<sub>2</sub> and CH<sub>4</sub> were found to be less than  $9.7 \times 10^{10}$  and  $3.4 \times 10^{10}$  molecule cm<sup>-3</sup>, respectively. This allowed to establish the upper limits for the branching ratios of the corresponding channels of reaction (1) at  $T = 900\text{K}$ :

$$k_{1e}/k_1 \leq 0.05$$

$$k_{1f}/k_1 \leq 0.02$$

**3.2. Secondary and side reactions.** As noted above, oxygen atoms were transformed to and detected as BrO radicals. The combined impact on the measured concentrations of BrO of the wall loss ( $(7\text{-}13)\text{ s}^{-1}$ ) and recombination reaction of the radicals (reaction 8) was  $\leq 10\%$  and was taken into account:



$$k_7 = 1.6 \times 10^{-12} \exp(210/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over } T = 230\text{-}390\text{K}.^{11}$$

Reaction of BrO with C<sub>2</sub>H<sub>4</sub> (present in the reactor in high concentrations, Table 1) also has little effect on [BrO], considering the upper limits of the rate constant of this reaction determined in the present study:

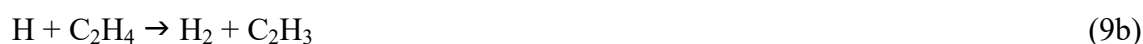


$$k_8 \leq 4.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } T = 299 \text{ K},$$

$$k_8 \leq 5.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } T = 897 \text{ K}.$$

We have not carried out special experiments concerning the fate of other radicals formed in reaction (1) (which are co-products of the species we have detected): CH<sub>2</sub>CHO, CH<sub>3</sub>CO, HCO, and CH<sub>2</sub>. Most probably, they react with Br<sub>2</sub> molecules present in high concentration in the reactor, forming corresponding brominated organic compounds. What is important in the frame of this study is that these species (brominated or not) are expected to have very limited contribution on the parent mass peaks of the reaction products quantitatively monitored in this work: *m/z* = 30 (CH<sub>2</sub>O<sup>+</sup>), 80 (HBr<sup>+</sup>), 94 (CH<sub>3</sub>Br<sup>+</sup>).

Hydrogen atoms produced in reaction (1) react with Br<sub>2</sub> to form HBr, but can also react with another excess reactant, C<sub>2</sub>H<sub>4</sub>:



Under experimental conditions of the present study, the abstraction channel (9b) is negligible and reaction (9) is dominated by addition pathway (9a) with a rate constant of nearly 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.<sup>4</sup> Considering that the rate constant of reaction (2) is much higher (nearly 7 × 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup><sup>7,13</sup> at *T* = 298K, increasing with temperature<sup>7,13</sup>) and the concentration ratios [C<sub>2</sub>H<sub>4</sub>]/[Br<sub>2</sub>] used in the study (see Table 1), the H atom consumption in reaction (9) can be neglected. Additional evidence for the limited impact of reaction (9a) is the absence in reaction products of C<sub>2</sub>H<sub>5</sub>Br (*m/z* = 108/110) which would be probably formed in reaction of C<sub>2</sub>H<sub>5</sub> adduct radical with Br<sub>2</sub>.

Another point which needs to be discussed is the possible reactions of Br atoms present in the reactive system. Indeed, Br atoms are formed in reaction (4), and in reactions of Br<sub>2</sub> with various radicals produced in reaction (1). The concentration of Br atoms in the reactor is expected to be somewhat higher than initial concentration of oxygen atoms. The main side reaction where Br atoms can be involved is their reaction with C<sub>2</sub>H<sub>4</sub> which is present in the reactor in high concentrations:



$$k_{10} = 3.0 \times 10^{-33} \exp(730/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \quad (T = 233\text{-}320\text{K}, P = 0.5\text{-}2 \text{ Torr})^{14}$$

However, under experimental conditions of the study this reaction is slow and, in addition, the formed adduct-radical is unstable and decomposes back to reactants.<sup>14</sup> Another reaction which potentially could have an impact on the observed products of reaction (1) is the reaction of Br atoms with CH<sub>2</sub>O:



$$k_{11} = 7.7 \times 10^{-12} \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (T = 220\text{-}300\text{K})^{15}$$

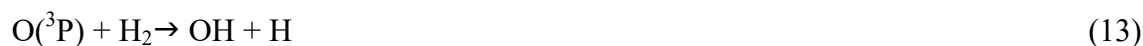
At low temperature edge of the *T*-range used the possible impact of reaction (11) is very limited considering relatively low initial concentrations of oxygen atoms used. No data for the reaction rate constant are available at high temperatures. Extrapolation of the existing measurements<sup>15</sup> to *T* = 900 K gives the values of the rate constant in the range (6.2-9.6) × 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Even with highest value of *k*<sub>11</sub> = 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> and maximal concentration of [O]<sub>0</sub> = 1.4 × 10<sup>12</sup> molecule cm<sup>-3</sup> the consumption of CH<sub>2</sub>O in reaction with Br at *T* = 900 K would be less than 5% (reaction time ≈ 3 ms). In addition, it can be noted that generally we have not observed any changes in the concentration of the recorded products of reaction (1) upon increase of the reaction time (up to 12ms).

Finally, we have checked for the presence in the reactor of electronically excited oxygen atoms O(<sup>1</sup>D), possibly formed in the microwave discharge of O<sub>2</sub>/He mixture. For that, the

oxygen atoms formed in the microwave discharge and introduced into the reactor (at  $T = 298$  K) through movable injector were transformed to BrO in reaction (4) with an excess of Br<sub>2</sub> ( $\approx 4 \times 10^{13}$  molecule cm<sup>-3</sup>), in the presence and in the absence of H<sub>2</sub> ( $\approx 5 \times 10^{14}$  molecule cm<sup>-3</sup>) in the reactor. In the absence of H<sub>2</sub> in the reactive system, the observed concentration of BrO correspond to the initial concentration of oxygen atoms ( $[O(^3P)] + [O(^1D)]$ ). In the presence of H<sub>2</sub>, the O(<sup>1</sup>D) atoms, if available, would selectively react with H<sub>2</sub>:



$$k_{12} = 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (T = 298 \text{ K})^{16}$$



$$k_{13} = 9.4 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (T = 298 \text{ K})^4$$

The products of reaction (12) would be scavenged by Br<sub>2</sub> via reactions (2) and (14), forming HBr and HOBr, respectively:



$$k_{14} = 4.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (T = 298 \text{ K})^{17}$$

Reaction of OH radicals with H<sub>2</sub> is too slow to compete with reaction (14):



$$k_{15} = 8.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (T = 298 \text{ K})^4$$

It was observed that addition of H<sub>2</sub> in the reactor (i) did not affect the concentration of BrO and (ii) did not lead to the formation of detectable concentrations of HOBr or HBr: concentration of HOBr was estimated to be less than that of BrO by a factor of more than 200 which means that the content of O(<sup>1</sup>D) in the total concentration of oxygen atoms entering the reactor is less than 0.5%. Thus the impact of the possible presence of O(<sup>1</sup>D) on the measured distribution of the products of reaction (1) can be considered as negligible.

**3.3. Comparison with previous data.** The results of the previous quantitative studies of the products of reaction (1) at near room temperature are presented in Table 2. One can note that our data for H, CH<sub>3</sub> and H<sub>2</sub> forming channels are in good agreement with the most of previous studies and current recommendation.<sup>4</sup> Of particular note is a good agreement between the branching ratio data obtained from measurements of different co-products: H and CH<sub>2</sub>CHO, CH<sub>3</sub> and HCO, H<sub>2</sub> and CH<sub>2</sub>CO for channels (1a), (1c), (1e), respectively. The yield of H atoms measured in the present work corresponds to the sum of two channels, (1a) and (1b). However, considering the experimental data on CH<sub>2</sub>CHO yield<sup>18-19</sup> and theoretical considerations,<sup>20</sup> it can be attributed to channel (1a), channel (1b) being negligible, at least, at room temperature. Present data confirm that CH<sub>2</sub>O is an important product of reaction (1). The branching ratio for (1d) channel from this study agrees, in the range of quoted experimental uncertainties, with the data reported by Endo et al.<sup>18</sup> and Peeters et al.<sup>6,20</sup> and is somewhat higher than that of Bley et al.<sup>21</sup> In general, our results support current considerations that the two major reaction channels are (1a) and (1c), contributing to nearly 80-90% of the products. The remaining products are mainly accounted for by the formaldehyde forming channel (1d), whose inclusion in combustion models seems to be mandatory.

**Table 2. Summary of the Measurements of the Branching Ratios for O+C<sub>2</sub>H<sub>4</sub> Reaction at Near Room Temperature**

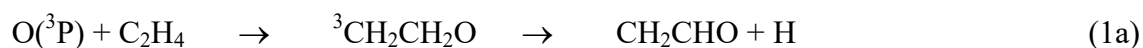
| Reference                           | <i>P</i> (Torr) | Branching ratio (detected product)           |   |                                    |                                       |  |
|-------------------------------------|-----------------|--|---|------------------------------------|---------------------------------------|--|
|                                     |                 | H+CH <sub>2</sub> CHO & H+CH <sub>3</sub> CO | CH <sub>3</sub> +HCO                      | CH <sub>2</sub> +CH <sub>2</sub> O | H <sub>2</sub> +CH <sub>2</sub> CO    | CH <sub>4</sub> +CO                    |
| Hunziker et al. <sup>19</sup>       | 40-760          | 0.36±0.04 (CH <sub>2</sub> CHO)              | (0.52-0.58)±0.06 (HCO)                    |                                    |                                       |  |
| Sridharan & Kaufman <sup>22</sup>   | 0.4-0.6         | 0.79±0.14 (H)                                |   |                                    |                                       |  |
| Endo et al. <sup>18</sup>           | 0.03            | 0.4±0.1 (CH <sub>2</sub> CHO)                | 0.5±0.1 (HCO)                             | 0.10±0.05 (CH <sub>2</sub> O)      | < 0.024 (CH <sub>2</sub> CO)          |  |
| Smalley et al. <sup>23</sup>        | 50-100          | 0.27±0.05 (H)                                |   |                                    |                                       |  |
| Peeters & Maes <sup>6,20</sup>      | 0.7-5           | 0.38±0.10 (H)                                | 0.48±0.10 (CH <sub>3</sub> )              | 0.10±0.05 (CH <sub>2</sub> )       | 0.04 (CH <sub>2</sub> CO)             |  |
| Bley et al. <sup>21</sup>           | 0.75-3          | 0.5±0.1 (H)                                  | 0.44±0.15 (HCO)                           | 0.06±0.03 (CH <sub>2</sub> )       |                                       |  |
| Knyazev et al. <sup>24</sup>        | 1-12.1          | <sup>a</sup> 0.73-0.49 (H)                   |   |                                    |                                       |  |
| Anastasi et al. <sup>25</sup>       | 760             |  | <sup>b</sup> 0.70±0.05 (CH <sub>3</sub> ) |                                    |                                       |  |
| Miyoshi et al. <sup>26</sup>        | 1.5-4           |  | 0.53±0.04 (CH <sub>3</sub> )              |                                    | 0.019±0.001 (CH <sub>2</sub> CO)      |  |
| Current recommendation <sup>4</sup> |                 | 0.35±0.05                                    | 0.6±0.1                                   |                                    | 0.05±0.1                              |  |
| This work                           | 1-8             | 0.31±0.05 (H)                                | 0.53±0.09 (CH <sub>3</sub> )              | 0.17±0.03 (CH <sub>2</sub> O)      | <sup>c</sup> ≤ 0.05 (H <sub>2</sub> ) | <sup>c</sup> ≤ 0.02 (CH <sub>4</sub> ) |

<sup>a</sup> yield decreasing with pressure

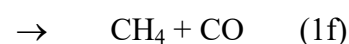
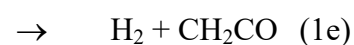
<sup>b</sup> un upper limit of 0.03 was reported for HCO yield.

<sup>c</sup> measured at *T* = 900 K.

The main features of the mechanism of the reaction  $O+C_2H_4$  are currently understood<sup>20,27</sup> and involve, as a first step, an addition of  $O(^3P)$  to double bond of ethylene to form a triplet biradical  $^3CH_2-CH_2O$ . The biradical can either dissociate directly to produce  $H + CH_2CHO$  and  $CH_2 + CH_2O$ ,



or intersystem cross to the singlet state followed by H-atom migration leading to formation of a hot acetaldehyde  $CH_3CHO^*$ . The latter then dissociates to form mainly methyl radicals and other reaction products:



The products of adduct stabilization, acetaldehyde and ethylene oxide, were also observed at pressures between 5 and 70 bar.<sup>21</sup> Given the good agreement between the branching ratios measured under different pressures (Table 2), the collisional stabilization can be regarded as negligible at pressures below 1 bar, and the branching ratios reported for bimolecular channels can be considered as pressure independent for  $P = 0.03 - 760$  Torr (Table 2).

Miyoshi et al.<sup>26</sup> measured the yields of two co-products of reaction (1c),  $CH_3$  and  $HCO$ , and found that the ratio of the  $HCO$  yield to that of  $CH_3$  is less than unity and increases upon increase of pressure: from 0.7 at 1 Torr to 0.9 at 4 Torr of helium. This observation was interpreted in the frame of mechanism suggesting that some fraction of  $HCO$  formed in reaction (1c) is hot ( $HCO^*$ ) and may partly decompose at low pressures:





Dissociation of HCO\*, being an additional source of H atoms, may result in overestimation of the H-atom yield and its dependence on total pressure in the reactor. As shown above (Figure 4), we have not observed any pressure effect on the yield of hydrogen atoms in the pressure range 1 - 8 Torr of He. Probably, this relatively weak effect is masked by the uncertainty of the measurements. Another possibility is partial scavenge of HCO\* in reaction with Br<sub>2</sub>, similarly to reaction of non-excited HCO:



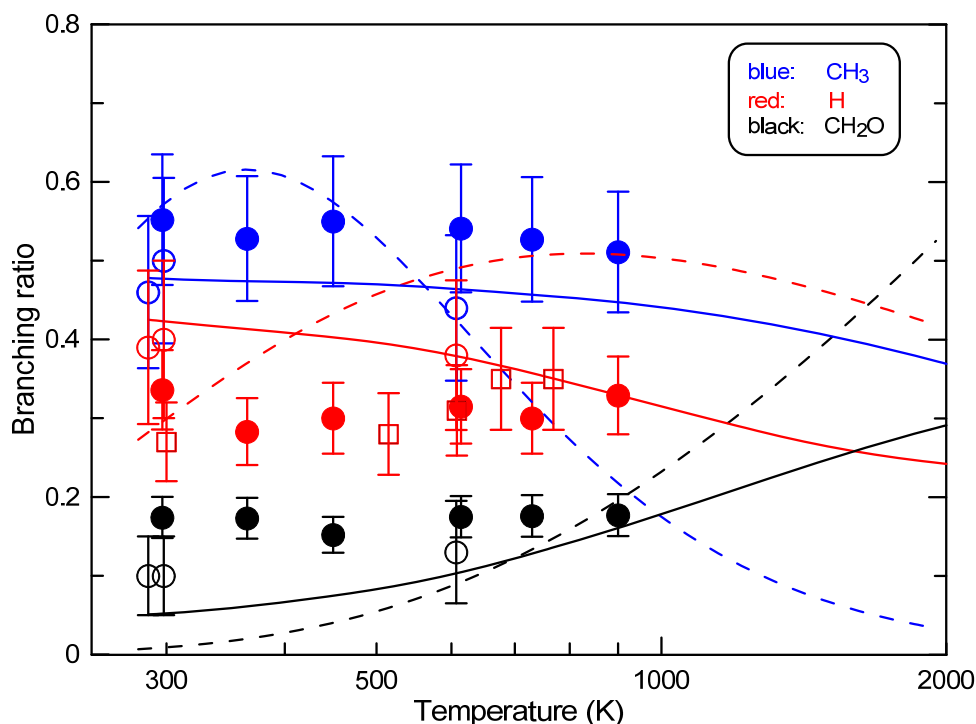
$$k_{18} = 1.58 \times 10^{-11} \exp(447/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (T = 296-669 \text{ K})^{28}$$

The available temperature dependent data for the branching ratios of different channels of reaction (1) is presented in Table 3 (theoretical branching fractions<sup>20,29</sup> are given for T-range from room temperature to 900K in order to simplify the comparison with the present data). The yield of the reaction products as a function of temperature has been reported only in two kinetic studies. Smalley et al.<sup>23</sup> in their flash photolysis-resonance fluorescence study have measured the H-atom yield in the temperature range 300-769 K. Very slight increase of the yield with increasing temperature was observed (from  $0.27 \pm 0.05$  at  $T = 300\text{K}$  to  $0.35$  at  $T = 769 \text{ K}$ ). Peeters and coworkers<sup>6,20</sup> measured the yields of the reaction products at two temperatures, 287 and 607K, and reported a small influence of temperature within this range. All the results of temperature dependence studies of the products of reaction (1) are shown in Figure 5 in line with theoretical calculations.

**Table 3. Summary of the Measured and Calculated Branching Ratios for O+C<sub>2</sub>H<sub>4</sub> Reaction as a Function of Temperature**

| Reference                                | <i>T</i> (K)            | H+CH <sub>2</sub> CHO &<br>H+CH <sub>3</sub> CO                   | Branching ratio (detected product)        |   |                                    |                           |
|--|-------------------------|---|---|---|------------------------------------|---------------------------|
|  |                         |   | CH <sub>3</sub> +HCO                      | CH <sub>2</sub> +CH <sub>2</sub> O                        | H <sub>2</sub> +CH <sub>2</sub> CO | CH <sub>4</sub> +CO       |
|  |                         |   | Experiment                                |   |                                    |                           |
| Smalley et al. <sup>23</sup>             | 300-769                 | 0.27-0.35 (H)   |   |   |                                    |                           |
| Peeters & Maes <sup>6,20</sup>           | 287-607                 | 0.38±0.10 (H)   | 0.48±0.10 (CH <sub>3</sub> )              | 0.10±0.05 (CH <sub>2</sub> )                              | 0.04 (CH <sub>2</sub> CO)          |                           |
| This work                                | 297-900                 | 0.31±0.05 (H)   | 0.53±0.09 (CH <sub>3</sub> )              | 0.17±0.03 (CH <sub>2</sub> O)                             | ≤ 0.05 (H <sub>2</sub> )           | ≤ 0.02 (CH <sub>4</sub> ) |
| Schmoltner et al. <sup>30</sup>          | <sup>a</sup> CMB (6.0)  | <sup>b</sup> 0.23-0.38 (CH <sub>2</sub> CHO)                      | <sup>b</sup> 0.62-.077 (CH <sub>3</sub> ) |   |                                    |                           |
| <sup>c</sup> Morton et al. <sup>31</sup> | <sup>a</sup> CMB (6.0)  | <sup>b</sup> 0.62 ±0.05 (CH <sub>2</sub> CHO)                     | <sup>b</sup> 0.38±0.05 (CH <sub>3</sub> ) |   |                                    |                           |
| Fu et al. <sup>3</sup>                   | <sup>a</sup> CMB (8.4)  | 0.30±0.06 (CH <sub>2</sub> CHO)<br>0.03±0.01 (CH <sub>3</sub> CO) | 0.34±0.09 (CH <sub>3</sub> )              | 0.20 ±0.05 (CH <sub>2</sub> )                             | 0.13±0.04 (CH <sub>2</sub> CO)     |                           |
| Balucani et al. <sup>32</sup>            | <sup>a</sup> CMB (13.7) | 0.33±0.07 (CH <sub>2</sub> CHO)<br>0.02±0.01 (CH <sub>3</sub> CO) | 0.31±0.08 (CH <sub>3</sub> )              | 0.21 <sup>+0.02</sup> <sub>-0.08</sub> (CH <sub>2</sub> ) | 0.13±0.03 (CH <sub>2</sub> CO)     |                           |
|  |                         |   | Theory                                    |   |                                    |                           |
| <sup>d</sup> Nguyen et al. <sup>20</sup> | 287-900                 | 0.42-0.33 (H)   | 0.48-0.45                                 | 0.05-0.16   | 0.024-0.032                        | 0.023-0.030               |
| Li et al. <sup>29</sup>                  | 300-900                 | 0.30-0.51 (H)   | 0.57-0.22                                 | 0.01-0.20   | 0.035-0.016                        |                           |
| Fu et al. <sup>3</sup>                   | 8.4 kcal/mol            | 0.28 (CH <sub>2</sub> CHO)<br>0.10 (CH <sub>3</sub> CO)           | 0.49                                      | 0.08  | 0.05                               |                           |
| Balucani et al. <sup>32</sup>            | 13.7 kcal/mol           | 0.33 (CH <sub>2</sub> CHO)<br>0.07 (CH <sub>3</sub> CO)           | 0.45                                      | 0.11  | 0.04                               |                           |

<sup>a</sup> crossed molecular beam scattering experiments (collision energy in kcal/mol)  
<sup>b</sup> calculated under assumption that no other reaction channel contributes, as only the ratio between these two channels was determined  
<sup>c</sup> revised data from Schmoltner et al.<sup>30</sup>  
<sup>d</sup> calculated using the value of 45:55 for the ratio of triplet and singlet yields



**Figure 5.** Branching ratio for  $\text{CH}_3$ , H and  $\text{CH}_2\text{O}$  forming channels ((1c), (1a)+(1b) and (1d), respectively) of reaction (1) as a function of temperature. Experimental data: filled circles - this study; open circles – refs. 6,20; squares – ref. 23. Theory: continuous lines – ref. 20; dashed lines – ref. 29.

Both the absolute values of the branching ratios from two previous experimental studies and the absence of the significant temperature dependence are in good agreement with the results of the present work. One can note also a fairly good agreement between the experimental data and theoretical calculations of Nguyen et al.<sup>20</sup> (continuous lines in Figure 5) especially with regard to the weak dependence of the branching fractions on temperature. On the contrary, the branching fractions calculated in very recent theoretical study of Li et al.<sup>29</sup> (dashed lines in Figure 5) significantly deviate from the experimental results. In contrast to our experiments, the theoretical calculations predict significant decrease of the  $\text{CH}_3$  yield and increase of the  $\text{CH}_2\text{O}$  and H-atom yields with increasing temperature. Li et al.<sup>29</sup> attributed the differences in branching fractions calculated in their study and that of Nguyen et al.<sup>20</sup> to the treatment of intersystem crossing. In the study of Nguyen et al.<sup>20</sup> the calculations were performed separately for the triplet and singlet channels and the overall branching fractions were

obtained assuming independent of temperature ratio of singlet to triplet products of 55:45. In contrast, the calculations of Li et al.<sup>29</sup> predict increased importance of the triplet product channels at elevated temperatures. The experimental data from the present study provide the independent of temperature value of nearly 57:43 for the ratio of singlet and triplet yields in the temperature range 298-900K, supporting the assumption of Nguyen et al.<sup>20</sup>

Although the comparison of the present data with crossed molecular beam (CMB) experiments is somewhat difficult (problem to relate temperature and collision energy), our results seem to agree with CMB data for H-atom and CH<sub>2</sub>O yields, however some disagreement is observed for the yields of CH<sub>3</sub> and H<sub>2</sub>. Regarding the temperature dependence, the absence of the appreciable impact of temperature on the branching ratios observed in the present study is in line with the results of CBM experiments and theoretical calculations which have shown that the collision energy ( $E_c = 8.4\text{-}13.7 \text{ kcal mol}^{-1}$ ) does not play a significant role in the branching ratios of five product channels, (1a) – (1e).<sup>3,32</sup> One can emphasize also a good agreement between the absolute values of the branching ratios from the present study with theoretical calculations of Fu et al.<sup>3</sup> and Balucani et al.<sup>32</sup>

The observed in general good agreement of the branching fractions determined in this work with the most of the experimental data available in the literature indicates the suitability and reliability of the applied experimental approach especially regarding the conversion of the active reaction products to stable species in reactions with Br<sub>2</sub>. We intend to apply this method for investigation of the products distribution in reactions of O(<sup>3</sup>P) atoms with propene and higher alkenes.

## CONCLUSIONS

We have reported the results of an experimental study of the products of the multichannel reaction of triplet oxygen atoms with ethylene. This is the first detailed and systematic study of the distribution of the reaction products as a function of temperature over an extended temperature range 298 – 900 K. The yields of three main reaction products, H-atom, CH<sub>3</sub> radical and CH<sub>2</sub>O, were measured (0.31, 0.53 and 0.17, respectively) and found to be independent (within 15-20% uncertainty) of temperature. The upper limits were determined for the yields of the minor reaction products: 0.05 and 0.02 for H<sub>2</sub> and CH<sub>4</sub>, respectively. Our results support current considerations that the two major reaction pathways (H and CH<sub>3</sub> forming) contribute to nearly 80-90% of the products, the remaining products being accounted for by the formaldehyde forming channel. The branching ratios determined in this work are in good agreement with the most of the experimental data available in the literature, however, do not support the latest theoretical predictions.

## ASSOCIATED CONTENT

### Supporting Information.

Concentration of products of reaction (1) as a function of consumed concentration of oxygen atoms at  $T = 365$  (Figure S1), 450 (Figure S2) and 730K (Figure S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## TOC GRAPHIC

