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Reaction of $O(^3P)$ with C_3H_6: Yield of the Reaction Products as a Function of Temperature

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ABSTRACT

Reaction of oxygen atoms with propene is an important step in combustion processes particularly affecting the profiles of intermediate species and flame speed. The relative importance of different pathways of this multichannel reaction at different temperatures represents significant theoretical interest and is essential for modeling combustion systems. In the present work, we report the first experimental investigation of the products of the $O(^3P)+C_3H_6$ reaction over an extended temperature range (298 – 905 K). Using a low pressure flow reactor combined with a quadrupole mass spectrometer, the yields of the five reaction products, H-atom, CH_3, C_2H_5, CH_2O and OH were determined as a function of temperature between 298 and 905 K: $0.0064\times(T/298)^{2.74}\exp(765/T)$, $1.41\times(T/298)^{-1.0}\exp(-335/T)$, $0.92\times(T/298)^{-1.41}\exp(-381/T)$, $0.17\times(T/298)^{0.165}\exp(-36/T)$ and $0.0034\times(T/298)^{2.34}\exp(788/T)$, respectively (corresponding to the variation of the respective yields between 298 and 905 K in the ranges 0.08-0.31, 0.46-0.32, 0.26-0.12, 0.15-0.19 and 0.05-011), independent of pressure in the range (1 – 8) Torr of helium. For the yields of the minor reaction products, H_2 and CH_3CHO the upper limits were determined as 0.2 and 0.05, respectively. These results are compared with the experimental data and theoretical calculations available in the literature.

1. INTRODUCTION

Propene, like other small alkenes, being an important intermediate in the oxidation of hydrocarbons,[1] is one of the key species of the kinetic mechanisms in combustion chemistry. 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 propene with triplet oxygen is of great fundamental interest with regard to a complex mechanism with a variety of competitive reaction pathways:[2, 3]

$O+C_3H_6$	$\rightarrow$	$H+ CH_3CHCHO$	$\Delta H°_0$ = -17.2 kcal mol^{-1}	(1a)
	$\rightarrow$	$H+ CH_3COCH_2$	$\Delta H°_0$ = -18.3 kcal mol^{-1}	(1b)
	$\rightarrow$	CH_3+CH_2CHO	$\Delta H°_0$ = -25.1 kcal mol^{-1}	(1c)
	$\rightarrow$	CH_3+CH_3CO	$\Delta H°_0$ = -31.7 kcal mol^{-1}	(1d)
	$\rightarrow$	C_2H_5+HCO	$\Delta H°_0$ = -24.8 kcal mol^{-1}	(1e)
	$\rightarrow$	$CH_2O+ CH_3CH/C_2H_4$	$\Delta H°_0$ = -5.4/-76.3 kcal mol^{-1}	(1f)
	$\rightarrow$	H_2+CH_3CHCO	$\Delta H°_0$ = -78.8 kcal mol^{-1}	(1g)
	$\rightarrow$	CH_2+CH_3CHO	$\Delta H°_0$ = -10.7 kcal mol^{-1}	(1h)
	$\rightarrow$	C_3H_5+OH	$\Delta H°_0$ = -14.5 kcal mol^{-1}	(1i)
	$\rightarrow$	$CO+C_2H_6$	$\Delta H°_0$ = -110.8 kcal mol^{-1}	(1j)
	$\rightarrow$	CH_3CH_2CHO+M	$\Delta H°_0$ = -108.7 kcal mol^{-1}	(1k)
	$\rightarrow$	$CH_3CH(O)CH_2+M$	$\Delta H°_0$ = -87.4 kcal mol^{-1}	(1l)

The theoretical and practical interests to the reaction of O-atom with propene initiated an extensive research, experimental and theoretical, of this reactive system over the past few decades (refs. 3, 4 and references therein). Currently, the total reaction rate constant can be considered as well established over a wide temperature range extending from atmospheric temperatures to those in combustion.[4] As for the mechanism of this multichannel reaction, the

distribution of the reaction products as a function of temperature, to our knowledge, has never been studied. Determination of the primary reaction products and branching ratios for the different reaction channels as a function of temperature is of crucial importance for modeling combustion systems.

In this work, we report the results of the first study of the yields of all the main products of reaction (1) as a function of temperature in the range T = 298 – 905K.

2. EXPERIMENTAL

2.1. Flow reactor and experimental methods. Experiments were carried out in a discharge flow reactor using a modulated molecular beam electron impact ionization 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).[5, 6] The temperature in the reactor was measured with a *K*-type thermocouple positioned in the middle of the reactor in contact with its outer surface. A temperature gradient along the flow tube measured with a thermocouple inserted in the reactor through the movable injector was found to be less than 1% (see temperature profile in Figure 1).[6]

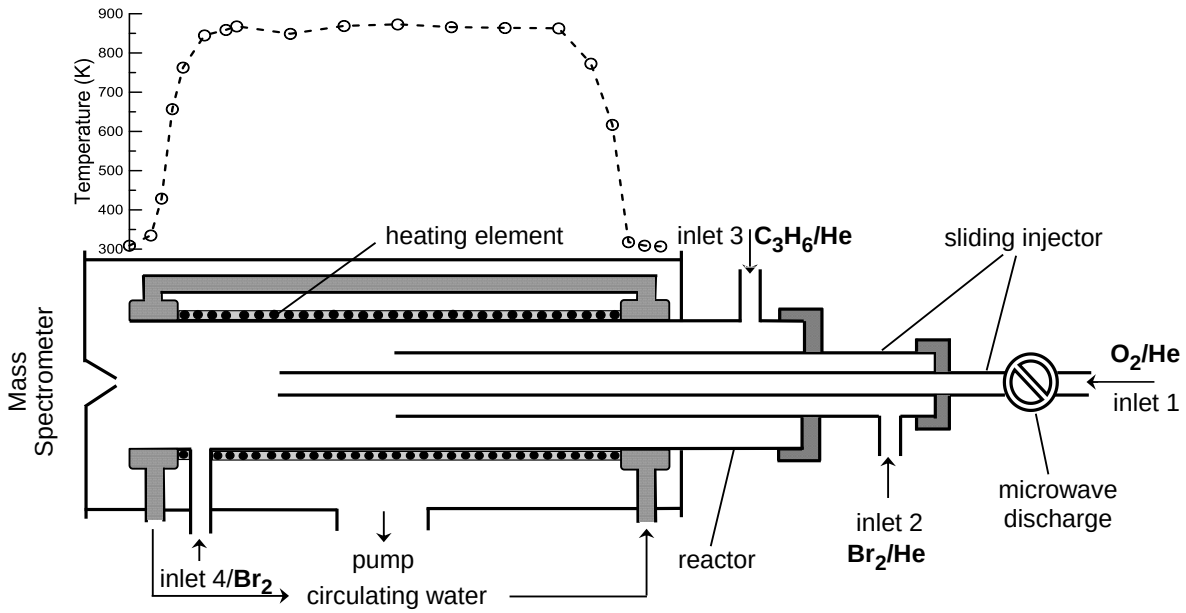

Figure 1. Diagram of the flow reactor.

The experimental approach applied for the measurements of the yields of the products of reaction (1) was similar to that we have used in our recent study of the products of the reaction of oxygen atoms with ethylene[5] and consisted in titration of oxygen atoms with a mixture of C_3H_6 and Br_2:

$$O + C_3H_6 \rightarrow \text{products} \quad (2)$$

$k_2 = 3.65\times10^{-18}\, T^{2.20} \exp(455/T)$ cm^{3}molecule^{-1}s^{-1} at T = (200 – 1200) K [4]

$$O + Br_2 \rightarrow BrO + Br \quad (3)$$

The rate constant of the reaction (3) is not well established: it is in the range (1.4 -2)$\times10^{-11}$ cm^{3}molecule^{-1}s^{-1} at room temperature and has negative temperature dependence.[7, 8] In the presence of Br_2 in the reactive system, the chemically active products of reaction (1), atoms and radicals, once formed, are rapidly scavenged by Br_2:

$$H + Br_2 \rightarrow HBr + Br \quad (4)$$

$k_4 = 6.7\times10^{-10}\exp(-680/T)$ cm^{3}molecule^{-1}s^{-1} (T = 214-295K)[9]

$$CH_3 + Br_2 \rightarrow CH_3Br + Br \quad (5)$$

$k_5 = 2.0\times10^{-11}\exp(197/T)$ cm^{3}molecule^{-1}s^{-1} (T = 296-532K)[10]

$$C_2H_5 + Br_2 \rightarrow C_2H_5Br + Br \quad (6)$$

$k_6 = 2.6\times10^{-11}\exp(414/T)$ cm^{3}molecule^{-1}s^{-1} (T = 298-532K)[10]

$$C_3H_5 + Br_2 \rightarrow Br + CH_2CHCH_2Br \quad (7)$$

$k_7 = 4.8\times10^{-12}\exp(808/T)$ cm^{3}molecule^{-1}s^{-1} (T = 298-532K)[11]

$$OH + Br_2 \rightarrow HOBr + Br \quad (8)$$

$k_8 = 1.85\times10^{-9}T^{-0.66}$ cm^{3}molecule^{-1}s^{-1} (T = 297-766K)[12]

Although no reliable rate constant data are available for reactions (4) - (7) at high temperatures, it is obvious that at the highest temperatures (T = 905K) of the present study

they are fast enough to rapidly scavenge corresponding active species in the presence of sufficiently high concentration of Br_2, $[Br_2] = (3 - 5)\times10^{13}$ molecule cm^{-3}. This configuration of the reactor allows one not only to transform the labile reaction products into the stable species which can be easily and in an absolute way recorded with a mass spectrometer but also, and as a consequence, to avoid rapid secondary reactions of the radicals formed in reaction (1) with oxygen atoms. In this way, in addition to formaldehyde which was detected directly at its parent peak (m/z = 30, CH_2O^+), we were able to detect three other major products of reaction (1), H, CH_3 and C_2H_5 at m/z = 80/82 (HBr^+), 94/96 (CH_3Br^+) and 108/110 ($C_2H_5Br^+$), respectively, and also OH and C_3H_5 at m/z = 96/98 ($HOBr^+$) and 120/122 ($C_3H_5Br^+$). Concerning the fate of other radicals formed in reaction (1) (which are co-products of the major reaction products we have detected), CH_3CHCHO, CH_3COCH_2, CH_2CHO, CH_3CO and HCO, most probably, they react with Br_2 molecules present in high concentration in the reactor, forming corresponding brominated organic compounds. What is important in the frame of this study is that all these species (brominated or not), except HCO, are expected to have very limited contribution on the parent mass peaks of the reaction products quantitatively monitored in this work. HCO radical formed in reaction (1e) is supposed to be rapidly scavenged in reaction with Br_2:

$$HCO + Br_2 \rightarrow HC(O)Br + Br \qquad (9)$$

$k_9 = 1.58\times10^{-11}\exp(447/T)$ $cm^3 molecule^{-1} s^{-1}$ (T = 296-669 K) [13]

The parent peaks of formyl bromide, HC(O)Br, coincide with those of C_2H_5Br (m/z = 108/110), that potentially could lead to an overestimation of the yield measured for C_2H_5. We failed to find a mass spectra of HC(O)Br in available mass spectrometry data bases. However, the analysis of the mass spectra of the compounds of similar structure, acetyl bromide ($CH_3C(O)Br$) and propionyl bromide ($C_2H_5C(O)Br$) shows that the intensity of their parent peaks is extremely low, at least, by a factor of 1000 lower than that of the most intensive

fragment peaks at m/z = 43 and 57, respectively.[14] One can expect a similar picture for mass spectra of HC(O)Br and, as a consequence, a negligible contribution of this species at m/z = 108/110. Our recent work[5] on the study of the reaction of O atoms with C_2H_4 using similar experimental approach and experimental conditions (concentrations of Br_2 and O) seems to support this assumption. Indeed, we have measured the branching ratio of nearly 50% for CH_3+HCO forming channel of this reaction (upon detection of CH_3Br) and have not found any signal at m/z = 108/110 despite the anticipated presence of HCO in a reactive system.

Oxygen atoms were generated from the microwave discharge in O_2/He mixtures and introduced into the reactor through the movable injector (Figure 1). In the absence of propene in the reactor, the oxygen atoms are stoichiometrically converted to BrO in reaction with Br_2 and detected at m/z=95/97 as BrO^+. Concentration of BrO measured in this case corresponds to the initial concentration of O-atoms. The concentration of O consumed in reaction with C_3H_6 was determined as a difference between initial concentration of BrO (recorded in the absence of C_3H_6) and concentration of BrO recorded in the presence of both Br_2 and C_3H_6 in the reactor. The measurements were carried out under the following experimental conditions: $[Br_2] = (3 - 5)\times10^{13}$ molecule cm^{-3}, concentrations of C_3H_6 are shown in Table 1, residence time in the temperature controlled zone of (5 – 10) ms.

One of the inconveniences of the described experimental approach is the generation in the reactor of Br atoms (in reactions (3) – (9)) and BrO radicals (in reaction 3) upon titration of oxygen atoms with C_3H_6 and Br_2 simultaneously present in the reactor. Both Br and BrO can react with the excess reactant C_3H_6 (especially at high temperatures) and potentially impact the results of the measurements (see below). For this reason, in some experiments, we have used the configuration where oxygen atoms reacted with C_3H_6 in the main reactor and Br_2 was added at the end of the reactor (through inlet 4, Figure 1). In order to minimize the possible secondary reactions of oxygen atoms relatively high concentrations of propene (13.0, 8.0, 6.5,

and 5.7×10^{13} molecule cm^{-3} at T = 363, 606, 738 and 905K, respectively) and short reaction times (3-3.5 ms) were used in these experiments. Under these conditions, almost complete consumption (more than 90%) of O atoms in reaction with C_3H_6 was observed. In this configuration, the impact of the reactions of Br and BrO with propene is limited, because Br and BrO are formed in the relatively low temperature zone (see temperature profile in Figure 1) and, in addition, the concentration of BrO is less than 10% of the initial concentration of oxygen atoms.

Absolute calibration of BrO signals was realized by chemical conversion of BrO to NO_2 through reaction (10) conducted in excess of NO (flowed through inlet 4) with subsequent detection of NO_2 formed ($[BrO]_0 = [NO_2]_{formed}$):

$$BrO + NO \rightarrow Br + NO_2 \qquad (10)$$

$k_{10} = 8.7\times10^{-12} \exp(260/T)$ $cm^3 molecule^{-1} s^{-1}$ over T = 220-430K.[15]

BrO radicals in the calibration experiments were formed through reaction (3). The absolute concentrations of NO_2 as well as of other stable species (Br_2, C_3H_6, CH_3Br, C_2H_5Br, C_3H_5Br, H_2, CH_3CHO, $C_2H_5ONO_2$) 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 (4) in excess of Br_2. In this case, H-atoms produced in a microwave discharge of H_2/He mixtures were titrated with Br_2 and concentration of HBr was determined from the consumed fraction of Br_2, $[HBr] = \Delta[Br_2]$. Chemical conversion of OH to HOBr via reaction (8) was used for the measurements of the absolute concentrations of the OH radicals:[16, 17] $[OH] = [HOBr] = \Delta[Br_2]$. OH in these experiments was generated in fast reaction of H atoms with excess NO_2. 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_2O in water inside the flow tube, and recording the parent mass peak intensity of CH_2O at m/z = 30. The integrated area of the mass

spectrometric signals corresponding to known total number of CH_2O molecules injected into the reactor allowed the determination of the calibration factor. Another alternative method used for absolute calibrations of CH_2O and CH_3Br consisted in thermal decomposition of ethyl nitrate (at T ≥ 500K) in the presence of Br_2 in the reactor:

$$CH_3CH_2ONO_2\ (+M) \rightarrow CH_3 + CH_2O + NO_2\ (+M) \qquad (11)$$

(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, NO_2, CH_2O and CH_3 (converted to CH_3Br in presence of Br_2) was observed and absolute concentrations of the species could be determined in accordance with: $[CH_3Br] = [CH_2O] = [NO_2] = [C_2H_5ONO_2]_0$. The results of this calibration method were in good agreement (within 10-15%) with that by injection of CH_2O and measurements of $[CH_3Br]$ and $[NO_2]$ from their calibrated mixtures.

Ethyl nitrate was synthesized in the laboratory through reaction of ethanol with H_2SO_4:HNO_3 (1:1) mixture.[18, 19] Gas chromatographic analysis of $C_2H_5ONO_2$ 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 trap; O_2 > 99.995% (Alphagaz); H_2 > 99.998% (Alphagaz); C_3H_6 >99.99% (Phillips); Br_2 >99.99% (Aldrich); CH_3Br > 99% (Aldrich); CH_2CH_3Br > 99% (Aldrich); NO_2 > 99% (Alphagaz); NO > 99% (Alphagaz); CH_2O, 36.5 wt. % in H_2O (Sigma-Aldrich).

2.2. 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 ((7-13) s^{-1}) and recombination reaction of the radicals (reaction 12) was ≤ 10% and was taken into account:

$$BrO + BrO \rightarrow \text{products} \qquad (12)$$

$k_{12} = 1.6\times10^{-12} \exp(210/T)$ $cm^3 molecule^{-1} s^{-1}$ over T = 230-390K.[15]

Another reaction leading to consumption of BrO (particularly, at high temperatures) was the reaction of BrO with C_3H_6:

$$BrO + C_3H_6 \rightarrow \text{products} \quad (13)$$

The detailed measurements of the rate constant of this reaction were out of scope of the present study. However, in separate experiments, where BrO was formed in the movable injector through reaction (3) and reacted with C_3H_6 in the main reactor, we have verified that (i) the rate of BrO loss was proportional to the concentration of C_3H_6 with roughly estimated effective rate constant increasing with temperature from ~5×10^{-15} at T = 298K to ~10^{-12} $cm^3molecule^{-1}s^{-1}$ at T = 905 K and (ii) reaction $BrO+C_3H_6$ did not produce any species which could interfere with those which were monitored as products of reaction (1) in branching experiments (HBr, CH_3Br, C_2H_5Br, C_3H_5Br, HOBr, CH_2O). These observations indicate that reaction (13) does not affect the measurement of the products of reaction (1) and has only limited impact (which was taken into account) on the concentration of BrO. It can be noted that consumption of BrO is not necessarily due to elementary reaction (13): it can result from a complex mechanism in $Br/BrO/Br_2/C_3H_6$ mixture.

Hydrogen atoms produced in reaction (1) react with Br_2 to form HBr, but can also react with another excess reactant, C_3H_6:

$$H + C_3H_6\ (+M) \rightarrow \text{adduct}\ (+M) \quad (14a)$$

$$H + C_3H_6 \rightarrow H_2 + C_3H_5 \quad (14b)$$

Under the experimental conditions of the present study, the abstraction channel (14b) is negligible and reaction (14) is dominated by addition pathway (14a) with a rate constant increasing with temperature in the range (2 - 4)$\times10^{-12}$ $cm^3molecule^{-1}s^{-1}$.[20] In experiments with Br_2 present in the main reactor, considering that the rate constant of the reaction (4) is much higher (nearly 7×10^{-11} $cm^3molecule^{-1}s^{-1}$ [9] at T = 298K, increasing with temperature[9, 21]) and the concentration ratio $[C_3H_6]/[Br_2] \leq 4$ used in the study, the H atom consumption in reaction

(14) can be neglected. Additional evidence for the limited impact of reaction (14a) is the absence in reaction products of C_3H_7Br (m/z = 122/124) which would be formed in reaction of C_3H_7 adduct radical with Br_2. On the other hand, the signal at m/z = 122/124 was observed in the absence of Br_2 in the main reactor (Br_2 being introduced through inlet 4), indicating the consumption of H atoms in the secondary reaction with C_3H_6. This was the reason we have not measured the yield of H atoms in this configuration of the chemical system.

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 (3), and in reactions of Br_2 with various radicals produced in reaction (1). The concentration of Br atoms in the reactor is expected to be somewhat higher than the initial concentration of oxygen atoms. The main side reaction where Br atoms can be involved is their reaction with C_3H_6 which is present in the reactor in high concentrations:

$$Br + C_3H_6 + M \rightarrow C_3H_6Br + M \quad (15a)$$

$k_{15a} = 3.8\times10^{-33}\exp(1200/T)$ cm^{6}molecule^{-2}s^{-1} (T = 233-320K, P = 0.5–2 Torr)[22]

$$Br + C_3H_6 \rightarrow HBr + CH_2CHCH_2 \quad (15b)$$

$k_{15b} = 8.15\times10^{-13}\exp(-1250/T)$ cm^{3}molecule^{-1}s^{-1} (T = 233-320K)[22]

In the context of the present study, the relevant channel is channel (15b): firstly, this is the dominant channel of reaction (15) at low pressures of the study and, secondly, it can directly impact the measurements of the yield of H atoms (detected as HBr). In presence of Br_2 in the reactor, the co-product of HBr in reaction (15b), C_3H_5 radical, is rapidly transformed to allyl bromide, C_3H_5Br, via reaction (7). This secondary formation of both C_3H_5Br (monitored at m/z =120 as $C_3H_5Br^+$) and HBr was observed experimentally: the concentrations of these species were found to increase with increase of the reaction time (O atoms being totally removed from the reactive system by C_3H_6/Br_2 mixture), while the concentrations of all the observed primary products did not change. In order to correct the observed concentration of

HBr for the secondary chemistry, the following procedure was used. First, it should be noted that C_3H_5 radical is also a potential primary product of reaction (1) which can be formed together with OH through channel (1i), i.e. the observed concentration of C_3H_5Br corresponds to the sum of the concentrations of C_3H_5 formed in reactions (1i) (primary) and (15b) (secondary). The concentration of primary C_3H_5 could be determined via the measurements of the concentration of the co-product of C_3H_5 in reaction (1i), OH radicals, considering that $[C_3H_5]_{primary}$ = [OH]. Then HBr formed in secondary reactions could be calculated as: $[HBr]_{secondary} = [C_3H_5]_{secondary} = [C_3H_5]_{observed}$ -[OH]. Calculated in this way secondary [HBr] was extracted from the observed total concentration of HBr. These corrections were in the range (5-40) %, depending on concentration of C_3H_6, reaction time and temperature.

Another reaction which potentially could have an impact on the observed products of reaction (1) is the reaction of Br atoms with CH_2O:

$$Br + CH_2O \rightarrow HBr + CHO \qquad (16)$$

$k_{16} = 7.7\times10^{-12}\exp(-580/T)$ $cm^3molecule^{-1}s^{-1}$ (T = 220-300K)[23]

Impact of this reaction seems to be negligible at all the temperatures of the study. If reaction (16) was operational one could expect decrease of the CH_2O yield upon increase of the initial concentration of O atoms (leading to increase of Br atoms in the reactor) which was not observed experimentally. In addition, we have not observed any changes in the concentration of CH_2O upon increase of the reaction time. Good agreement between the results obtained with addition of Br_2 in the reactor and at the end of the reactor (see above) is another indication of the limited impact of reaction (16) on the measured yield of CH_2O.

OH radicals, if formed in reaction (1), react with Br_2 in reaction (8) forming HOBr and with C_3H_6:

$$OH + C_3H_6 \rightarrow \text{products} \qquad (17)$$

Thus, the observed concentration of HOBr depends on the rate constants of the corresponding reactions and concentrations of Br_2 and C_3H_6:

$$[\mathrm{HOBr}]_{observed} = [\mathrm{OH}] \times \frac{k_8[\mathrm{Br_2}]}{k_8[\mathrm{Br_2}]+k_{17}[\mathrm{C_3H_6}]}$$

and concentration of OH radicals formed in reaction (1) can be calculated as:

$$[\mathrm{OH}] = [\mathrm{HOBr}]_{observed} \times (1 + \frac{k_{17}}{k_8}\frac{[\mathrm{C_3H_6}]}{[\mathrm{Br_2}]})$$

Thus to calculate the corrected yields of OH radicals one needs to know the value of the k_{17}/k_8 ratio under experimental conditions of the branching measurements: T = 298-905 K and P = 2 Torr (the rate of the addition channel of reaction (17) can be pressure dependent). Instead of analyzing the available literature data on the reactions (8) and (17), we preferred to directly measure the k_{17}/k_8 ratio under conditions used in the branching experiments, with regard to temperature, pressure and concentrations of Br_2 and C_3H_6. In experiments, OH reacted with Br_2/C_3H_6 mixture and partitioning of the radicals between reactions (8) and (17) was directly determined through monitoring of HOBr, product of reaction (8). Details of these experiments are presented in Supporting Information (SI). The following expression was obtained for the ratio of the rate constants of the reactions (8) and (17):

$$k_{17}/k_8 = 3.4\times10^{-4}\,(T/298)^{3.32}\exp(2138/T)$$

at P = 2 Torr of helium and in the temperature range T = 297-603 K. The values of k_{17}/k_8 calculated with above expression were used to correct the branching ratio data for OH measured at T = 298, 363, 433 and 606 K. For technical reasons (see SI) k_{17}/k_8 ratio was not measured at higher temperatures. To make corrections on OH branching data observed at T = 738 and 905 K, we used extrapolated values of k_{17}/k_8. Considering that the dependence of k_{17}/k_8 on temperature at T ≥ 600 K is not strong (Figure S2 in SI) and corrections on the yield of OH at T = 738K and 905 K are rather small (low k_{17}/k_8 and relatively low $[C_3H_6]/[Br_2]$) the additional uncertainty on the final data on OH yield due to extrapolation procedure is not expected to be significant. The correction factor on the observed concentration of HOBr

depended on the $[C_3H_6]/[Br_2]$ and k_{17}/k_8 ratios and decreased with temperature from 2.3 at T = 298K to (1.02-1.07) at T = 905 K.

Finally, in our previous paper we have checked for the presence in the reactor of electronically excited oxygen atoms $O(^1D)$, possibly formed in the microwave discharge of O_2/He mixture.[5] In particular, it was shown that the content of $O(^1D)$ in the total concentration of oxygen atoms entering the reactor is less than 0.5%, i.e. the possible impact of the presence of $O(^1D)$ on the measured distribution of the products of reaction (1) can be considered as negligible.

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 C_3H_6 and those of the four main reaction products formed: H, CH_3, C_2H_5 (detected as HBr, CH_3Br and C_2H_5Br, respectively), CH_2O and also of OH radicals (detected as HOBr). The measurements were carried out at 2 Torr total pressure of helium and temperature in the range 298 – 905 K. The results of all the measurements are shown in Figures 2-6 (and Figures S3-S5 in SI).

At T = 298 K the yield of the reaction products was measured as a function of pressure which was varied between 1 and 8 Torr of He. The results of the measurements presented in Figure 2 show that in the pressure range of the present study the yields of the major reaction products are independent of pressure.

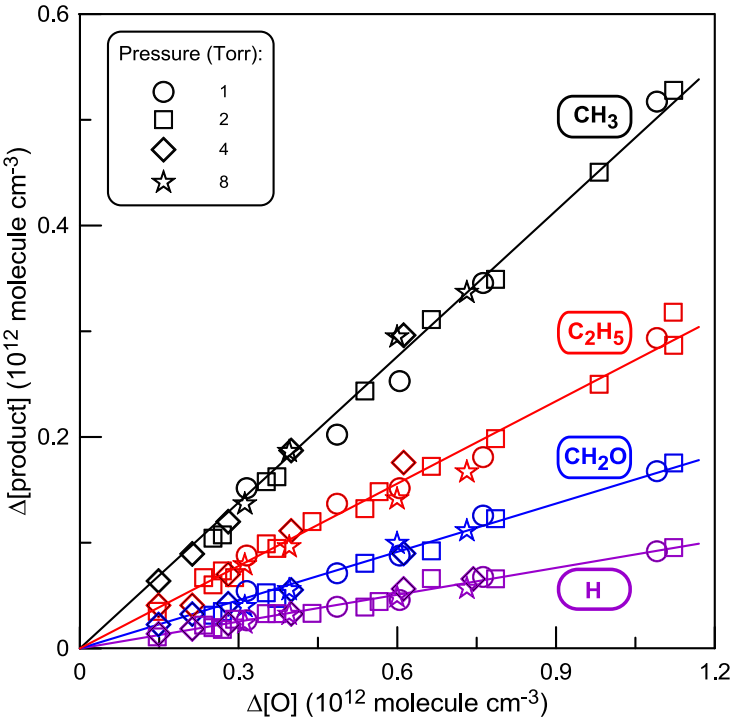

Figure 2. Concentration of products of reaction (1) as a function of consumed concentration of oxygen atoms measured at different pressures in the reactor: T = 298K, P = (1 – 8) Torr.

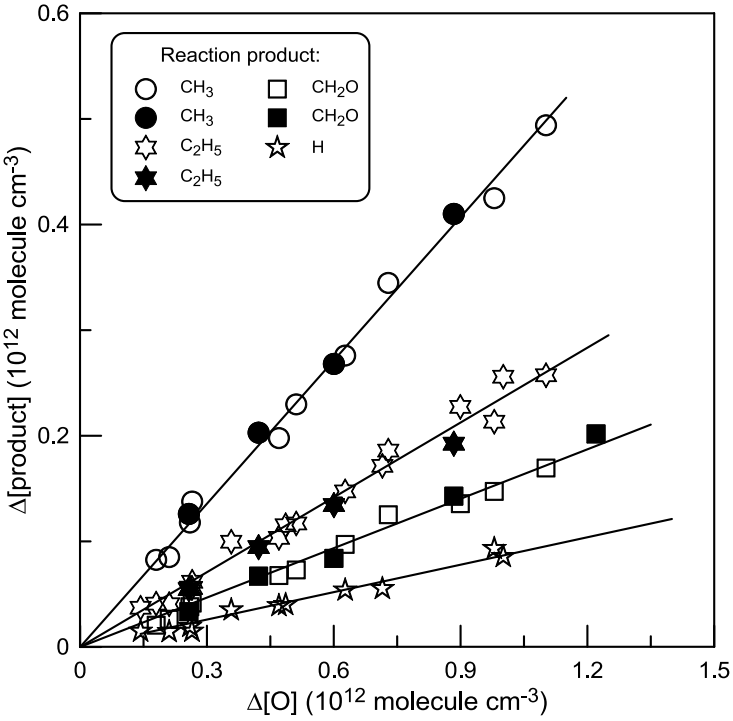

Figure 3. Concentration of products of reaction (1) as a function of consumed concentration of oxygen atoms: T = 363K, P = 2 Torr. Filled symbols represent the experiments with addition of Br_2 at the end of the reactor (see text).

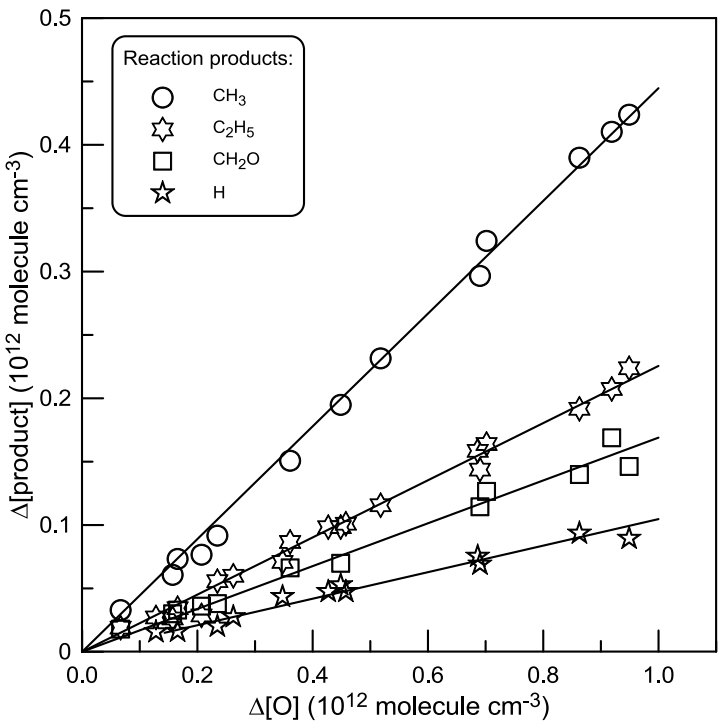

Figure 4. Concentration of products of reaction (1) as a function of consumed concentration of oxygen atoms: T = 433K, P = 2 Torr.

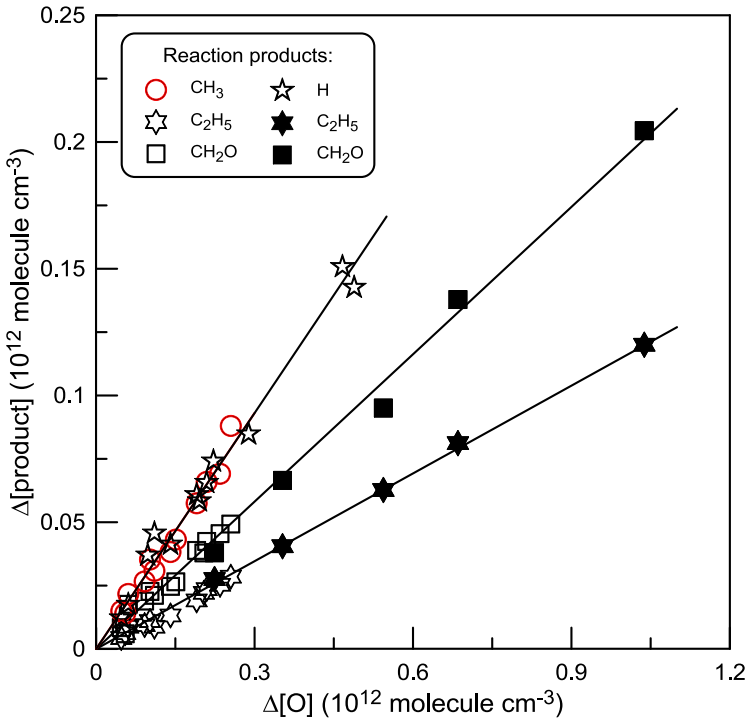

Figure 5. Concentration of products of reaction (1) as a function of consumed concentration of oxygen atoms: T = 905 K, P = 2 Torr. Filled symbols represent the experiments with addition of Br_2 at the end of the reactor (see text).

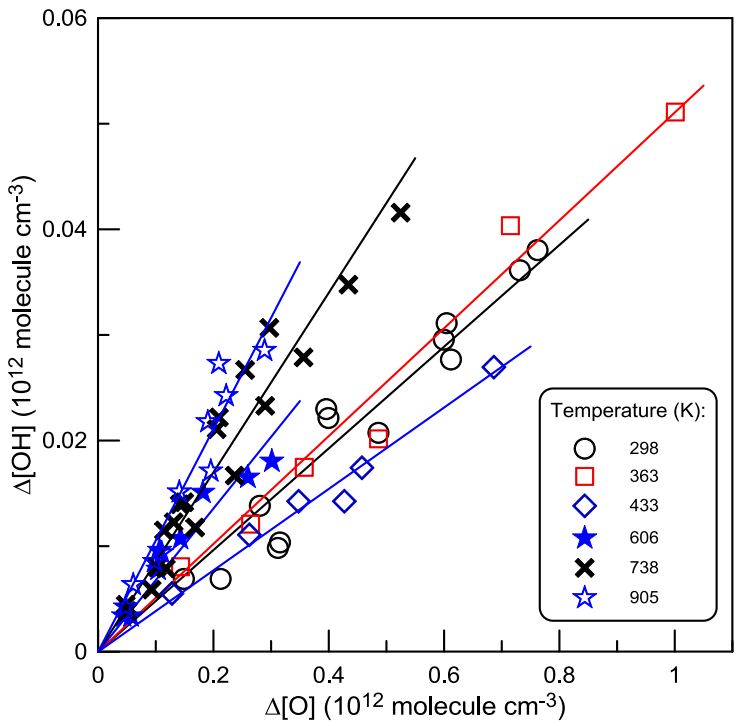

Figure 6. Concentration of OH radicals formed in reaction (1) as a function of consumed concentration of oxygen atoms at different temperatures: P = 2 Torr.

All the results obtained for the yields of H, CH_3, C_2H_5, CH_2O and OH (determined as slopes of the linear through origin fits to the experimental data in Figures 2-6 and S3-S5 in SI) are shown in Table 1. The estimated uncertainties on the yields of the reaction products are nearly 20% for CH_3, C_2H_5 and CH_2O, 25-30% for H atoms and 50% for OH radicals. The uncertainties are mainly due to combined errors on the determination of the absolute concentrations of the corresponding species and corrections applied to account for the secondary chemistry. Higher (compared with other species) uncertainty on the yield of OH radicals is due to additional error on the detection of very low concentrations of the radicals.

Table 1. Summary of the measurements of the yields of the products of reaction O+C_3H_6

T, K	$[C_3H_6]\times10^{-13}$ [a]	Yields of the reaction products					
		H	CH_3	C_2H_5	CH_2O	OH	Total [b]
298	4.5-12.0	0,085	0,460	0,260	0,152	0.048	1.005
363	9.0-12.0	0,087	0,452	0,236	0,156	0.051	0.982

433	5.7-8.5	0,105	0,444	0,226	0,169	0.039	0.983
606	3.0-4.5	0,153	0,410	0,180	0,176	0.068	0.987
738	1.6-2.8	0,222	0,363	0,167	0,194	0.085	1.031
905	0.7-1.7	0,310	0,310	0,115	0,194	0.105	1.034

[a] Units are molecule cm^{-3}; [b] sum of the yields of the five reaction products.

Temperature dependences of the branching ratios measured for all the observed products are shown in Figure 7. The fit of the experimental branching ratio data with the three parameter equation $A\times(T/298)^{B}\times\exp(E/T)$ (solid lines in Figure 7) provides the following expressions which can be recommended from the present study in the temperature range T = 298-905 K with conservative 50% uncertainty for k_{1i}/k_1 and nearly 20% for the rest of the data:

$$(k_{1a} + k_{1b})/k_1 = 0.0064\times(T/298)^{2.74}\exp(765/T)$$

$$(k_{1c} + k_{1d})/k_1 = 1.41\times(T/298)^{-1.0}\exp(-335/T)$$

$$k_{1e}/k_1 = 0.92\times(T/298)^{-1.41}\exp(-381/T)$$

$$k_{1f}/k_1 = 0.17\times(T/298)^{0.165}\exp(-36/T)$$

$$k_{1i}/k_1 = 0.0034\times(T/298)^{2.34}\exp(788/T)$$

The sum of the branching ratios measured for the five products of reaction (1) (last column in Table 1) is nearly 1 in the whole temperature range of the study, indicating that all the major reaction products were addressed in the measurements.

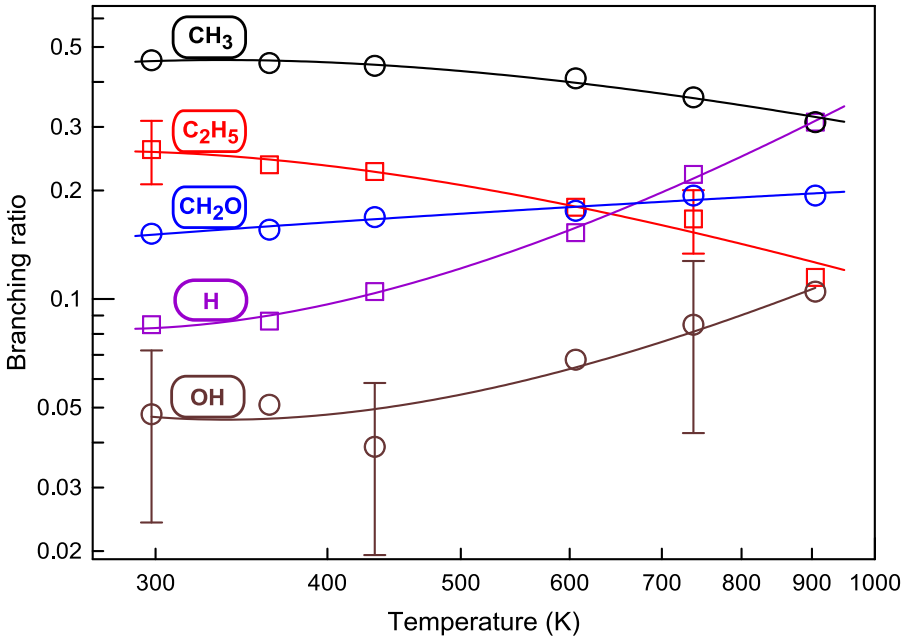

Figure 7. Branching ratios of the H, CH_3, C_2H_5, CH_2O and OH forming channels of reaction (1) as a function of temperature. The error bars represent typical nearly 20% (50% for OH radicals) uncertainty of the measurements.

The branching ratios for the minor channels (1g) and (1h) were explored in separate experiments carried out at T = 298, 730 and 905 K and 2 Torr total pressure. The corresponding targeted products were H_2 and CH_3CHO. From the lack of the formation of the measurable concentrations of these species upon consumption of O-atoms in reaction with C_3H_6 the upper limits for the branching ratios of the corresponding channels of reaction (1) were derived:

$k_{1g}/k_1 \leq 0.20$

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

in the temperature range T = (298-905) K. High background signal at m/z = 2 (H_2^+) prevented a more precise estimation of the upper limit for the branching ratio of the H_2 forming channel (1g).

3.2. Reaction mechanism. The formation of the four main products of reaction (1) observed in the present study (H, CH_3, C_2H_5 and CH_2O) can be described within the reaction mechanism developed in previous studies, especially in very recent theoretical work.[3] The

initial step of the reaction of ground state oxygen atom with propene is an electrophilic addition of $O(^3P)$ onto the C=C bond on both the terminal and central C atom, forming a triplet bi-radicals CH_3CHCH_2O and CH_3CHOCH_2, respectively. These intermediates can decompose directly leading to formation of H, CH_3 and CH_2O:

$$O(^3P) + C_3H_6 \rightarrow {}^3C_3H_6O \rightarrow H + CH_3CHCHO \quad (1a)$$

$$\rightarrow H + CH_3COCH_2 \quad (1b)$$

$$\rightarrow CH_3 + CH_2CHO \quad (1c)$$

$$\rightarrow CH_2O + CH_3CH/C_2H_4 \quad (1f)$$

Leonori et al.[3] in crossed molecular beam experiments (with collision energy of 9.3 kcal mol^{-1}) have observed two isomeric C_3H_5O radicals, CH_3CHCHO (7%) and CH_3COCH_2 (5%) formed upon H atom elimination, which is an experimental evidence of the addition of oxygen to both the terminal and central carbon atoms of propene. On the other hand, the theoretical calculations carried out by the same authors predict that H atom is produced mostly via C-H bond cleavage in CH_3CHCH_2O intermediate (channel (1a)). In contrast, the CH_3 forming channel was calculated to proceed mainly via addition of O to the central carbon atom. The decomposition of the intermediate triplet bi-radical CH_3CHCH_2O can also proceed through CH_2O and CH_3CH forming channel (1f).

The initially formed triplet bi-radicals can undergo intersystem crossing (ISC) to form a singlet bi-radicals followed by 1,2 H-atom migration leading to formation of a hot propanal $CH_3CH_2CHO^*$ (or acetone) which decomposes to a variety of final products, in particular, corresponding to two main channels:

$${}^3C_3H_6O \rightarrow {}^1C_3H_6O \rightarrow CH_3CH_2CHO^* \ (CH_3C(O)CH_3^*) \rightarrow CH_3 + CH_2CHO \quad (1c)$$

$$\rightarrow CH_3 + CH_3CO \quad (1d)$$

$$\rightarrow C_2H_5 + HCO \quad (1e)$$

According to the calculations of Leonori et al.,[3] the C_2H_5 + HCO forming pathway proceeds entirely on the singlet PES through decomposition of propanal. The excited propanal can also dissociate to form CH_3 and CH_2CHO. In fact, Leonori et al.[3] identified three reaction routes contributing to the production of CH_3: one (1/3 of total production at T = 300 K and 70% at collision energy of 9.3 kcal mol^{-1}) proceeding on the triplet surface and two others (2/3 of total production at T = 300 K and 30% at collision energy of 9.3 kcal mol^{-1}) on the singlet one through decomposition of hot propanal and acetone (channels 1c and 1d, respectively).

Considering the partitioning of CH_3 formed on triplet and singlet PES and 2-3% branching ratio for minor H_2 producing singlet channels,[3] the ISC extent of nearly 60 and 25% at T = 300 and 900 K, respectively, can be inferred from the branching ratio data measured in the present study. This result is in good agreement with RRKM calculations of Leonori et al.[3] predicting an extent of ISC which decreases from 60 to 20% upon increase of temperature (collision energy) from T = 300 K to E_c = 9.3 kcal mol^{-1} due to reduced lifetime of the triplet bi-radical and, as a result, lower probability of intersystem crossing at higher temperatures.

3.3. Comparison with previous studies. Products of reaction (1) at room temperature have been explored in several previous studies (Table 2), although the absolute measurements of the branching fractions are very rare. Kanofsky & Gutman[24] in their crossed molecular beams study using photoionization mass spectrometry classified the observed reaction products into three categories: major (CH_3, CHO and C_2H_5), with ion signals greater than 15% of the largest one; minor (CH_3CO, CH_2O, C_3H_4O and C_3H_6O), with ion signals less than 15% of the largest one; apparently absent (C_3H_5O, CH_2). Blumenberg et al.[25] analyzed the products of reaction (1) using mass spectrometry with energy-tunable electron impact ionization and reported the upper limits for CH_2O and H_2 yields, as well as the relative branching ratios for methyl and ethyl radical forming channels (Table 2). These results are in

good qualitative agreement with the present ones with regard to the fact that CH_3 and C_2H_5 are the main products of reaction (1) at room temperature.

Hunziker et al.[26] in their photochemical modulation spectroscopy study of the primary products of reaction (1) reported the yield of CH_2CHO (channel 1c) decreasing with increase of pressure, starting with ≈29% at 40 Torr and approaching the value of ≈19% at 760 Torr. The authors proposed two reaction paths forming CH_2CHO: a pressure-independent component which is responsible for the asymptotic high pressure yields of 0.19 and a pressure-dependent one. Koda et al.[27] using microwave absorption spectroscopy monitored the time evolutions of vinoxy, HCO, and CH_2O in reaction (1). The fraction of vinoxy production was found to be 0.29 ± 0.15 at total pressure of 30 mTorr. By comparing the initial rate of production of CH_2CHO and HCO, the authors have determined the relative yield of vinoxy vs HCO (channel (1d) vs (1c)) as 1:(1.39±0.18). In the present study, we have measured the total yield of methyl radicals (reactions 1c and 1d), whereas the vinoxy fractions measured by Hunziker et al.[26] and Koda et al.[27] correspond to the channel (1c). In accordance with theoretical calculations of Leonori et al.,[3] channel (1d) accounts for 43% of the total methyl production. Applying this to the total CH_3 yield measured in the present work, one gets 0.26 ± 0.05 for the branching fraction of vinoxy forming channel, in excellent agreement with two previous studies.

Table 2. Summary of the Measured and Calculated Branching Ratios for $O+C_3H_6$ Reaction

Reference	Branching ratio (detected product) [a]					
	$H+CH_3CHCHO$ $H+CH_3COCH_2$	CH_3+CH_2CHO CH_3+CH_3CO	C_2H_5+HCO	CH_2O+CH_3CH $CH_2O+C_2H_4$	H_2+CH_3CHCO	$OH+C_3H_5$
			Experiment			
Blumenberg et al.[25] (< 7.5 Torr)		(1.0) (CH_3) [b]	(0.95) (HCO)	< 0.05 (CH_2O/C_2H_4)	< 0.016 (H_2)	
Hunziker et al.[26] (40-760) Torr		0.29-0.19 (CH_2CHO)				
Koda et al.[27] (0.03 Torr)		0.29±0.15 (CH_2CHO) (1.0) (CH_2CHO)	(1.39±0.18) (HCO)			
Knyazev et al.[28] (0.09-11.2) Torr	0.46±0.11 (H)					
Anastasi et al.[29] (1 atm)		0.15±0.01 (CH_3) 0.12±0.03 (CH_2CHO)	< 0.03 (HCO)			
Min et al.[30] (0.5 Torr)			0.05±0.02 (HCO)			
Savee et al.[31] (4 Torr)	[0.085] [c]	(1.0) (CH_3) [0.41]	(0.91±0.30) (C_2H_5) [0.37±0.12]	(0.27±0.18) (C_2H_4) [0.11±0.07]	(0.05±0.04) (CH_3CHCO) [0.020±0.016]	
This work (1 – 8 Torr)	0.085±0.02 (H)	0.46±0.09 (CH_3)	0.26±0.05 (C_2H_5)	0.15 ±0.03 (CH_2O)	< 0.2 (H_2)	0.05 (OH)
This work (905 K)	0.31±0.06 (H)	0.31±0.06 (CH_3)	0.11±0.03 (C_2H_5)	0.19 ±0.04 (CH_2O)	< 0.2 (H_2)	0.10 (OH)
Leonori et al.[3] CMB (9.3) [d]	0.07±0.02 0.05±0.02	0.32±0.10 (CH_3)	0.09±0.04 (C_2H_5)	0.44±0.15 (CH_2O)	0.03±0.015 (CH_3CHCO)	
			Theory			
Leonori et al.[3] (T = 300 K)	0.159 0.003	0.442	0.283	0.065 0	0.018	
Leonori et al.[3] (9.3 kcal/mol)	0.261 0.010	0.326	0.070	0.321 0	0.011	

[a] at room temperature, if *T* is not specified; [b] in parentheses, branching ratios relative to that of CH_3; [c] in square brackets, branching ratios calculated using H atom yield from the present work; [d] crossed molecular beam scattering experiments (collision energy in kcal mol^{-1})

Although the nearly 40% yield of HCO which can be calculated from the data reported by Koda et al.[27] is somewhat higher than that of C_2H_5 measured in the present work, agreement between the two studies seems to be satisfactory considering rather large experimental uncertainties. The relatively low yields of methyl radicals (0.15 ± 0.01) and CH_2CHO (0.12 ± 0.03) measured by Anastasi et al.[29] at atmospheric pressure seem to reflect the pressure dependence reported by Hunziker et al.[26] The formyl radical was also searched for by Anastasi et al.[29] but was not detected, which placed an upper limit of 0.03 on its yield. Low yield of HCO (0.05±0.02) was also reported by Min et al.[30] who employed cavity ring-down spectroscopy to detect HCO in products of the reaction of $O(^3P)$ with different alkenes at total pressure of 0.5 Torr. The authors reported that HCO forming channel is the major channel of the reaction of O with ethene, a minor one of the reaction of O with propene, and not observable in the reaction of O with any other alkene, i.e. the branching ratio of HCO forming channel was found to decrease rapidly as the hydrocarbon chain of the alkene molecule lengthened.

The H-atom forming pathways of reaction (1) were explored in only one study by Knyazev et al.[28] The authors monitored H-atom formation in a discharge flow system using resonance fluorescence spectroscopy of O and H atoms at room temperature and in the pressure range 0.9-11.2 Torr. From the dependence of the concentration of H formed on the concentration of O consumed, the branching ratio for H atom producing channels was found to be 0.46 ± 0.11, independent of pressure. Channel (1a) was considered to be responsible for the H atom yield, channel (1b) being negligible. The H-atom yield reported by Knyazev et al.[28] is by a factor of nearly 5 higher than that measured in the present work. Washida et al.[32] using laser-induced fluorescence method examined formation of vinoxy radicals in the reaction of oxygen atom with propene at total pressure of 1.5 Torr of He. It was reported that the observed vinoxy radicals, CH_2CHO (channel 1c) and CH_3CHCHO (channel 1a),

correspond to major and minor routes of the reaction, respectively. These observations support the high yield of CH_3 and, especially, low yield of H observed in the present study at room temperature. Concerning the rather high H-atom yield reported by Knyazev et al.,[28] Leonori et al.[3] noted that the H-atom branching ratio determined in the same study for reaction of $O(^3P)$ with C_2H_4 was also largely higher than the currently accepted value, suggesting a possible systematic error in the measurements.

In the most extended room temperature study by Savee et al.,[31] the products of reaction (1) were examined by means of time-resolved multiplexed photoionization mass spectrometry at total pressure of 4 Torr. The authors determined the relative branching ratios of 1.00, 0.91 ± 0.30 and 0.05 ± 0.04 for the primary product CH_3, C_2H_5 + HCO and H_2 + CH_3CHCO forming channels, respectively. The branching ratio for CH_2O + C_2H_4 channel of (0.27±0.18) was also reported. Although the authors assigned the observed C_2H_4 as secondary product, the analysis of Leonori et al.[3] showed that CH_2O + CH_3CH/C_2H_4 could be potentially a primary reaction channel. In the study of Savee et al.[31] the H + CH_3CHCHO channel (1a) was not observed for technical reasons, so the authors used the value of Knyazev et al.[28] for the branching fraction of this channel (0.46±0.11) to convert the measured relative branching ratios to the absolute ones: 0.28±0.07, 0.25±0.07 and 0.05±0.04 for CH_3, C_2H_5 and H_2 forming channels, respectively. The respective absolute branching fractions calculated with our data for H atom forming channels (0.085±0.02) are shown in Table 2 (in square brackets). One can note a remarkable agreement (within quoted experimental uncertainties) between these data and those from the present work.

Concerning production of OH in reaction (1), previously Quandt et al.[33] in their laser induced fluorescence study under single-collision conditions have observed the OH radicals in the products of reactions of $O(^3P)$ with a series of alkenes including propene. Unfortunately, the absolute yields of the radicals were not reported.

To our knowledge, this is the first experimental study of the distribution of the products of reaction (1) as a function of temperature. The comparison of the present data with those from the recent crossed molecular beam (CMB) study[3] is somewhat difficult because of the complexity to relate temperature and collision energy. One can note that the branching ratio data obtained for CH_3 and C_2H_5 at the highest temperature (T = 905K) of the present work are very close to those from CBM experiments with collision energy of 9.3 kcal mol^{-1}, however the reported yields of H atoms and CH_2O are significantly different. Regarding the temperature dependence, the trends observed in the present study (increase of H and CH_2O and decrease of CH_3 and C_2H_5 yields with temperature) are in line with the theoretical predictions.[3] Moreover, the absolute values of the branching ratios measured in this work at T = 298 and 905 K are very close to some of those calculated by Leonori et al.[3] for T = 300 K and collision energy of 9.3 kcal mol^{-1}, respectively. However, it should be emphasized once again that the comparison of our data at T = 905 K with those of Leonori et al.[3] for collision energy of 9.3 kcal mol^{-1} is qualitative and not entirely correct, since the results from two studies correspond to different temperatures.

Finally, it should be noted that most of the available data on products of reactions (1) were obtained at low total pressures (≤ 11 Torr), where collisional stabilization is expected to be unimportant. Although Savee et al.[31] observed several isomers of C_3H_6O at 4 Torr total pressure, they were attributed to be due to secondary reactions. At high pressures the collisional stabilization channels (1k) and (1l) leading to formation of propanal (CH_3CH_2CHO) and methyloxirane ($CH_3CH(O)CH_2$), respectively, may be important and even dominant. In this respect, additional high pressure studies of the products of reaction (1) are needed in order to be included in the combustion models.

CONCLUSIONS

We have reported the results of an experimental study of the products of the multichannel reaction of triplet oxygen atoms with propene. This is the first study of the distribution of the reaction products as a function of temperature over an extended temperature range. The yields of five reaction products, H, CH_3, C_2H_5, CH_2O and OH, were determined at T = (298 – 905) K and found to be independent of pressure in the range (1 – 8) Torr. It was found in particular that the yields of CH_3 and C_2H_5 radicals decrease with temperature while those of H-atom, OH radical and CH_2O increase. Our results support current considerations that the extent of intersystem crossing decreases upon increase of temperature. The reported product data need to be extended to higher pressures for safe use in combustion models and seem to represent an interesting basis for further theoretical developments.

ASSOCIATED CONTENT

Supporting Information.

Measurements of the k_{17}/k_8 ratio; concentration of products of reaction (1) as a function of consumed concentration of oxygen atoms at T = 606 (Figures S3 and S4) and 738 K (Figure S5). This material is available free of charge via the Internet at http://pubs.acs.org.

ACKNOWLEDGEMENT

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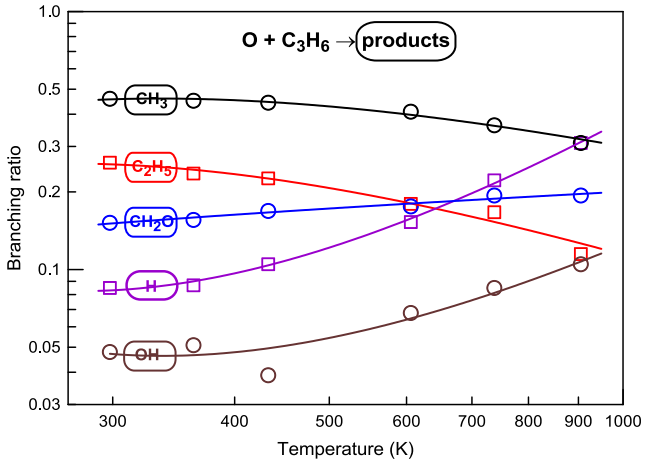
TOC Graphic


O + C3H6 → products
CH3
C2H5
CH2O
H
OH
Branching ratio
1.0
0.5
0.3
0.2
0.1
0.05
0.03
300
400
500
600
700
800
900
1000
Temperature (K)

Supporting Information

Reaction of $O(^3P)$ with C_3H_6: Yield of the Reaction Products as a Function of Temperature

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Number of Tables: 1

Number of Figures: 5

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Measurements of the k_{17}/k_8 ratio

In these experiments a fast titration of the initial concentration of OH radicals, $[OH]_0$, by a mixture of excess propene and Br_2 was performed,

$$OH + Br_2 \rightarrow HOBr + Br \quad (8)$$

$$OH + C_3H_6 \rightarrow \text{products} \quad (17)$$

and the yield of HOBr as a function of the $[C_3H_6]/[Br_2]$ ratio was measured. OH radicals formed in reaction of hydrogen atoms with excess NO_2 (~10^{13} molecule cm^{-3}) were introduced into the reactor through the movable injector. The concentration of HOBr formed was defined by the fraction of $[OH]_0$ reacting with Br_2:

$$[\mathrm{HOBr}] = \frac{k_8[\mathrm{Br_2}]}{k_8[\mathrm{Br_2}]+k_{17}[\mathrm{C_3H_6}]} \times [\mathrm{OH}]_0$$

Considering the derived expression,

$$\frac{[\mathrm{OH}]_0}{[\mathrm{HOBr}]} - 1 = \frac{k_{17}[\mathrm{C_{10}H_{16}}]}{k_8[\mathrm{Br_2}]} \quad \text{(I)},$$

k_{17}/k_8 could be obtained by plotting ($[OH]_0/[HOBr]$ - 1) as a function of the $[C_3H_6]/[Br_2]$ ratio. It can be noted that this method did not need absolute calibration of the mass-spectrometric signals for OH radicals and HOBr because the initial concentration of OH could be expressed as HOBr signal in the absence of propene, when OH is titrated with an excess of Br_2. Thus, in the experiments, only the HOBr signal was detected, first in the propene-free system, corresponding to $[OH]_0$, and then in the Br_2 and C_3H_6-containing system, corresponding to the fraction of $[OH]_0$ reacted with Br_2. The concentration ranges of C_3H_6 used in these experiments are shown in Table S1, concentration of Br_2 being nearly 3×10^{13} molecule cm^{-3} in all the experiments.

Table S1. Experimental conditions and results of the relative measurements of k_{17} to k_8 ratio.

[a]no./exp.	T (K)	[b]$[C_3H_6]$	$[C_3H_6]/[Br_2]$	k_{17}/k_8
4	297	1.7-21.9	0.6-7.6	0.454
5	363	1.5-21.4	0.4-16.6	0.234
5	433	2.7-43.4	1.0-13.5	0.171
6	603	2.8-48.1	1.0-17.7	0.122

[a] Number of data points; [b] units of 10^{13} molecule cm^{-3}.

Experiments have been carried out at four temperatures between 297 and 603K. At higher temperatures the applied method was not operational: we have observed the formation of product at m/z = 96/98 (where HOBr was monitored as $HOBr^+$) in $C_3H_6/Br_2/NO_2$ system (with microwave discharge switched off). It was verified that the presence of each of the three compounds in the reactor was necessary for the appearance of this product. The identification of the product (HOBr or other species) as well as detailed study of the complex $C_3H_6/Br_2/NO_2$ chemical system at high temperatures was out of the scope of the present study. Thereby, we have limited the measurements of the k_{17}/k_8 ratio to maximal temperature of 603 K.

The experimental data observed at different temperatures are shown in Figures S1. According to equation (I), the slopes of the linear dependences in Figure S1 provide the k_{17}/k_8 ratios at different temperatures which are shown in Table S1.

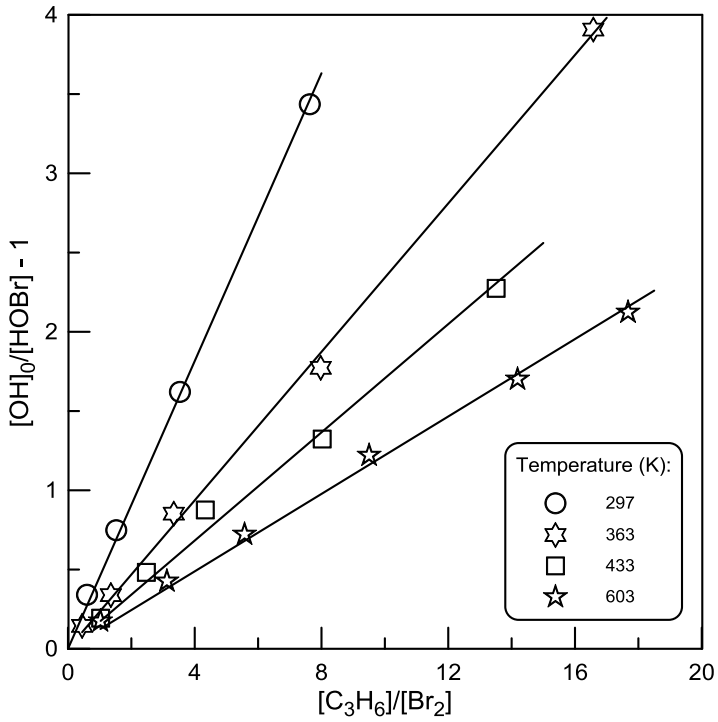

Figure S1. HOBr yield from OH titration with Br_2 + C_3H_6 mixtures at P = 2 Torr and different temperatures.

Temperature dependence of the ratio of the rate constants of the OH reactions with C_3H_6 and Br_2 is shown in Figure S2. The fit of the experimental data for k_{17}/k_8 with three parameter equation $A\times(T/298)^B\times\exp(E/T)$ (solid line in Figure S2) provides the following expression:

$$k_{17}/k_8 = 3.4\times10^{-4}\,(T/298)^{3.32}\exp(2138/T)$$

in the temperature range T = 297-603 K. The k_{17}/k_8 ratio decreases with increase of temperature and seems to reach a minimum at temperature of nearly 600 K. The extrapolation of k_{17}/k_8 to higher

temperatures using above expression is shown in Figure S2 as a dashed line. The extrapolated data show slow increase of the k_{17} to k_8 ratio at T > 600K.

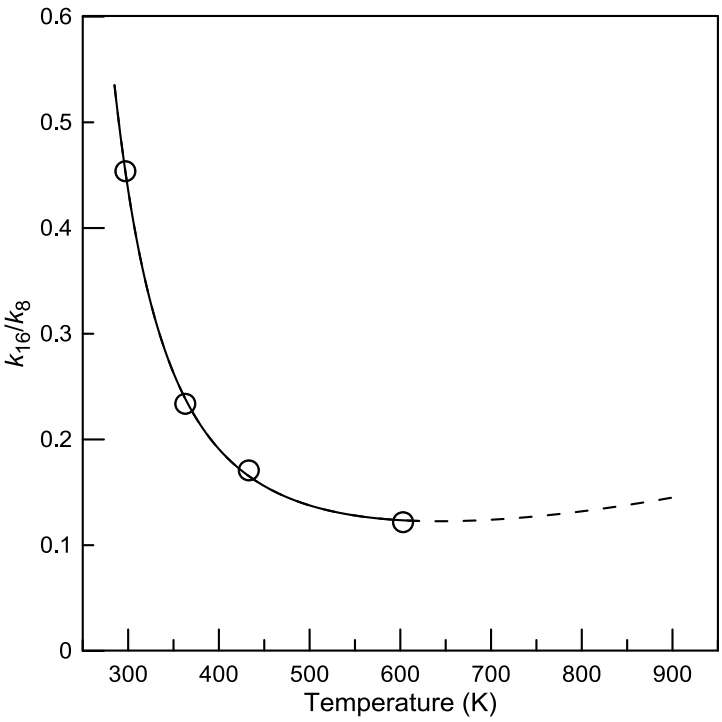

Figure S2. The ratio of the rate constants of the reactions of OH with C_3H_6 and Br_2 as a function of temperature.

Such behavior of the ratio of the rate constants is quite possible given that (i) at lower temperatures reaction of OH with propene is essentially addition reaction with negative temperature dependence and (ii) at higher temperatures H atom abstraction channel can become competitive. Unfortunately, this could not be verified in the present work.

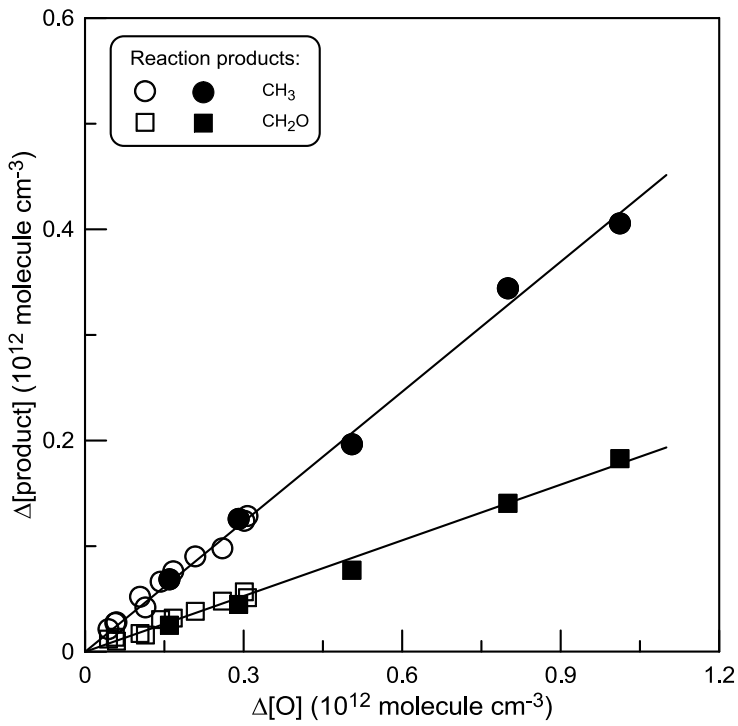

Figure S3. Concentrations of CH_3 and CH_2O formed in reaction (1) as a function of consumed concentration of oxygen atoms: T = 606 K, P = 2 Torr. Filled symbols represent the experiments with addition of Br_2 at the end of the reactor (see text).

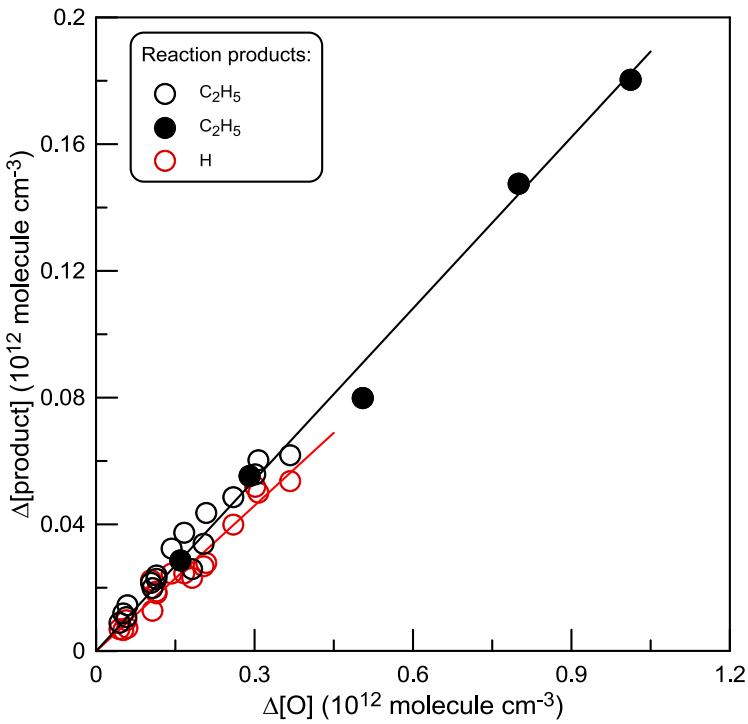

Figure S4. Concentrations of H atoms and C_2H_5 radicals formed in reaction (1) as a function of consumed concentration of oxygen atoms: T = 606 K, P = 2 Torr. Filled symbols represent the experiments with addition of Br_2 at the end of the reactor (see text).

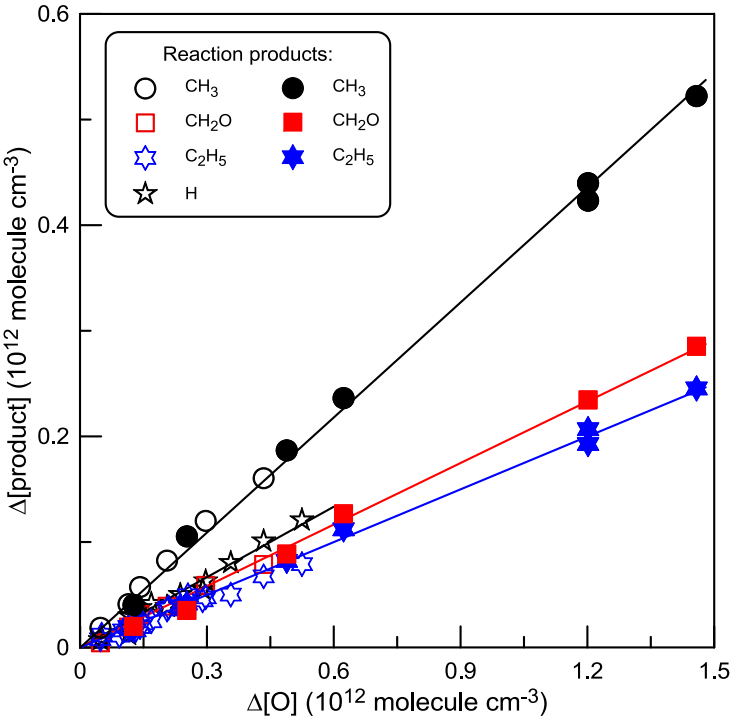

Figure S5. Concentration of products of reaction (1) as a function of consumed concentration of oxygen atoms: T = 738 K, P = 2 Torr. Filled symbols represent the experiments with addition of Br_2 at the end of the reactor (see text).