Relevance of the Channel Leading to Formaldehyde + Triplet Ethylidene in the O(^{3}P) + Propene Reaction under Combustion Conditions

Carlo Cavallotti*

Dipartimento di Chimica, Materiali e Ingegneria Chimica "Giulio Natta", Politecnico di Milano, 20131 Milano, Italy

Francesca Leonori, Nadia Balucani, Vaclav Nevrly,[§] Astrid Bergeat,[⊥] Stefano Falcinelli,[#] Gianmarco Vanuzzo, and Piergiorgio Casavecchia*

Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, 06123 Perugia, Italy

The reactions between ground-state ^{3}P oxygen atoms and unsaturated hydrocarbons have been the subject of extensive research during the last decades because of their important role in combustion and atmospheric chemistry (see refs 1 and 2 and references therein). The rate coefficients for most of them have been determined in kinetics experiments at room temperature or, better, at the temperature of relevance in combustion processes.[3] Much less is known, instead, of the chemical identity of the primary products and their branching ratios (BRs).[1] This piece of information is particularly relevant because the products of one elementary reaction are the reactants of a subsequent one in the complex scheme of elementary reactions that account for the global transformation.[1,4] In the case of relatively complex multichannel reactions, such as the title reaction, the primary products are not easy to guess. A significant complication is associated with the possible occurrence of intersystem crossing (ISC) from the triplet to the underlying singlet potential energy surface (PES), which might open other reaction channels not accessible on the triplet PES.[5−8] The occurrence of ISC and its extent as a function of temperature are not easy to predict, and only an accurate theoretical treatment or the experimental determination can quantify them. This has been well illustrated in the recent study of the O + C_2H_4 reaction[5,6] where ISC was found to be very efficient and to account for about 50% of the reaction products. Much less is known about the reactivity of O(^{3}P) with propene. Because of the presence of an additional methyl group, the reaction is much more complex; there are nine possible reaction channels (the reported enthalpies of reaction at 0 K are those calculated in this work; see below).

While there is good agreement for the value of the experimental global rate coefficient,[9−13] much less is known about the reaction mechanism and dynamics. Early crossed effusive beam experiments with a fixed photoionization mass spectrometer detector found that channels 3 and 4 were major observables routes, while channels 5 and 7 were minor routes, and channels 1, 2, and 8 were apparently absent.[14] Later studies in low-pressure reactors (crossed free jets and a laval nozzle reactor) using electron impact ionization mass spectrometric (MS) detection with tunable energy electrons (4.5−70 eV) confirmed that channels 3 and 4 are main channels, produced in comparable amounts.[15] Notably, this latter study was able to detect both mass 30 (formaldehyde) (by distinguishing it from NO) and 28 (ethylene) (by distinguishing it from CO);
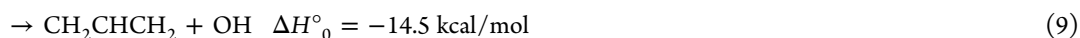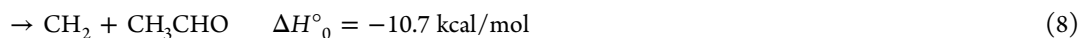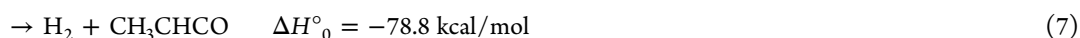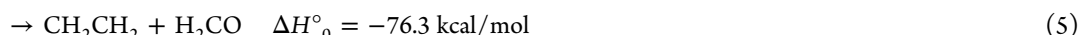
however, channel 5 was deemed to be a minor route. Neither study,[14,15] which correspond to a temperature of about 300 K, provided absolute BRs. Early kinetics microwave absorption spectroscopy studies[16] at room temperature quantified that channels 3 (C_2H_5 + HCO) and 4 (CH_3 + CH_2CHO) are indeed two important reaction channels, with branching fractions of 0.40 ± 0.05 and 0.29 ± 0.15, respectively; the CH_3 channel was concluded to be a major channel also by successive flow studies at 300 K.[17,18] Kinetics work at 300 K using resonance fluorescence spectroscopy of O and H atoms concluded that the CH_3CHCHO + H channel 1 accounts for 0.46 ± 0.11 of the reaction yield.[19] Very recently, Savee et al.

performed a kinetics study at 300 K using time-resolved photoionization MS detection with VUV synchrotron radiation.[20] The CH_3 and C_2H_5 forming channels were found to be the most important with a yield of 0.91 for the C_2H_5 channel relative to CH_3, while that of the H_2 + CH_3CHCO channel was 0.05. In that study, the H channels could not be detected for technical reasons, while the observed H_2CO + C_2H_4 channel was concluded to originate from secondary reactions, in this way not confirming the early conclusions[14,15] that this channel, although deemed minor, was taking place. The occurrence of some of these channels implies that triplet−singlet ISC is significant, but its extent could not be quantified.[20]

$$O(^3P) + CH_3CHCH_2 \rightarrow H + CH_3CHCHO \quad \Delta H^°_0 = -17.2 \text{ kcal/mol} \tag{1}$$

$$\rightarrow H + CH_3C(O)CH_2 \quad \Delta H^°_0 = -18.3 \text{ kcal/mol} \tag{2}$$

$$\rightarrow CH_3CH_2 + HCO \quad \Delta H^°_0 = -24.8 \text{ kcal/mol} \tag{3}$$

$$\rightarrow CH_3 + CH_2CHO \quad \Delta H^°_0 = -25.1 \text{ kcal/mol} \tag{4}$$

$$\rightarrow CH_2CH_2 + H_2CO \quad \Delta H^°_0 = -76.3 \text{ kcal/mol} \tag{5}$$

$$\rightarrow {}^3CHCH_3 + H_2CO \quad \Delta H^°_0 = -5.4 \text{ kcal/mol} \tag{6}$$

$$\rightarrow H_2 + CH_3CHCO \quad \Delta H^°_0 = -78.8 \text{ kcal/mol} \tag{7}$$

$$\rightarrow CH_2 + CH_3CHO \quad \Delta H^°_0 = -10.7 \text{ kcal/mol} \tag{8}$$

$$\rightarrow CH_2CHCH_2 + OH \quad \Delta H^°_0 = -14.5 \text{ kcal/mol} \tag{9}$$
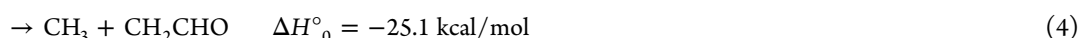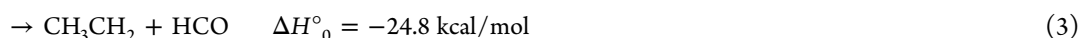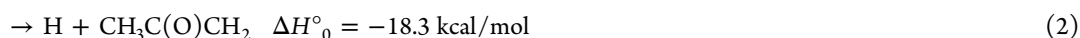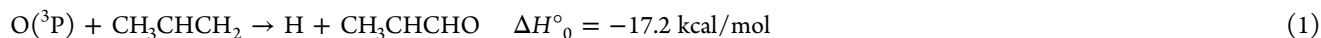
All of the mechanistic experimental studies described above were performed at essentially room temperature, while no branching data is available at combustion temperatures. The result is that at present, most combustion mechanisms describe the high-temperature reactivity of $O(^3P)$ + C_3H_6 using the total rate constant partitioned in reaction channels using (limited) room-temperature BRs.[13,21−23] As will be shown below, this approach can lead to substantial errors.

In this Letter, we report experimental and theoretical evidence that a new hitherto unidentified channel, that is, channel 6 leading to $^3CHCH_3$ + H_2CO, is an important reaction channel, the yield of which strongly increases with temperature. While this reaction channel is the equivalent of the H_2CO + $^3CH_2$ channel observed in $O(^3P)$ + C_2H_4,[5,6] in $O(^3P)$ + C_3H_6, it had never been observed experimentally at combustion temperatures, neither considered to be important, although the early work showed that some H_2CO is formed at room temperature. Only recent RRKM predictions (without accounting for ISC) on an ab initio triplet PES gave a yield for it of about 5% at 300 K and about 24% at 1500 K (at a pressure of 0.001 Torr).[24] The observation that at combustion temperatures the reactions of $O(^3P)$ with alkenes lead to significant formation of formaldehyde, an important pollutant, is an unexpected result that can have significant practical implications. In addition, the $^3CH_3CH$ + H_2CO channel has never been included in combustion kinetics models so far, and its introduction may affect the model outcomes.

On the experimental front, we have employed the crossed molecular beam (CMB) technique with MS detection and time-of-flight (TOF) analysis, empowered with soft electron ionization.[25,26] The CMB-MS allows us to interrogate all energetically open channels on the same footing, a prerequisite

for deriving the BRs under well-defined E_c's.[1,6] In particular, the CMB-MS technique (i) permits one to carry out investigations under truly single-collision conditions, avoiding the potential complications of a multiple-collision environment; (ii) can verify unambiguously, on the basis of energy and linear momentum conservation, to which channel belongs a given product detected at a given m/z ratio; and (iii) can exploit the extent of the product recoil energy of a given channel to assess the presence or not of an exit potential barrier.[1,25,26] This experimental approach has been successfully used in our laboratory to study the reactions $O(^3P)$ + acetylene,[27] ethylene,[5,6] allene,[28] and methylacetylene.[29] The present experimental results clearly show that formaldehyde is a primary reaction product at E_c = 9.3 kcal/mol. However, we could not unambiguously disentangle the relative contributions from channel 5 (occurring only after ISC has taken place) or channel 6 (occurring on the triplet PES without ISC).

On the theoretical front, we have carried out high-level ab initio calculations to identify the main reaction channels on the triplet PES and to calculate the rate of ISC between the triplet and singlet PESs. Statistical computations of BRs, taking into account also the possibility of ISC, have been performed to determine which reaction pathway leads to the observed formation of formaldehyde and which of the two C_2H_4/CH_3CH isomers is predominantly formed.

The relevant experimental and computational details are reported as Supporting Information (SI) to this Letter, while a more complete description of the experimental and theoretical results relative to the other reaction channels will be the subject of a more detailed publication.

The employed CMB beam apparatus is described in the SI. Reactive signal was observed at m/z = 56, 55, 30, 29, 28, and 15

(TOF spectra were measured at all of these masses, while the product angular distributions could be measured only at m/z = 56, 55, 29, and 15 for signal-to-noise reasons). The usual analysis of the CMB results (see SI) leads to the identification of channels 1−7, while channels 8 and 9 are estimated to be negligible (<1−2%) under our experimental conditions. Following the procedure outlined by Schmoltner et al.[30] (recently applied also to the reactions $O(^3P) + C_2H_2$ and $O(^3P) + C_2H_4$),[5,6,27] from our experimental data, once the origin of the various ion signals is sorted out, the relative yield of each product can be derived from the relative apparent cross section obtained from the best-fit analysis of the laboratory (LAB) data, the estimated ionization cross section, and the measured total ion yield for a specific product. The quadrupole transmission has been also taken into account. The experimentally derived BR for the $^3CH_3CH/C_2H_4 + H_2CO$ channels is 0.44 ± 0.15 under the present experimental conditions.

The experimental evidence for the $^3CH_3CH + H_2CO$ reaction route comes from reactive signals detected at m/z = 30 (H_2CO^+), 29 ($HCO^+/C_2H_5^+$), and 28 ($CH_3CH^+/C_2H_4^+$). In Figure 1 is reported the LAB angular distributions measured
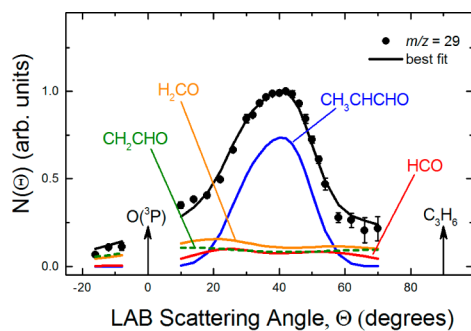

Figure 2. TOF distributions for m/z = 30 (at Θ_{CM} = 38°) and m/z = 29 (at Θ = 26°). Symbols are as those in Figure 1.

Figure 1. LAB angular distributions at m/z = 29 for the $O(^3P)$ + propene reaction at E_c = 9.3 kcal mol^{-1}. The solid black curves represent the calculated total angular distributions when using the best-fit CM functions for the relevant channels (those for the channels 5/6 are shown in Figure 3) (see the SI). The separate contributions to the calculated global LAB angular distributions are indicated with the formula of the corresponding product.

at m/z = 29 (as already said, it could not be determined at m/z = 30). The TOF distribution at the center-of-mass angle, Θ_{CM}, of 38° for m/z = 30 and that for m/z = 29 at Θ = 26° are shown in Figure 2. As can be seen, according to our analysis at m/z = 29, we have a contribution from H_2CO (which is known to strongly fragment to daughter ion HCO^+) from channels 5 and/or 6, from the parent ion of the formyl radical produced in channel 3, from the daughter ion of CH_2CHO (vinoxy, which is known[5,6] to fragment to HCO^+) formed in channel 4, and from the daughter ion HCO^+ of CH_3CHCHO from the H elimination channel 1 (see Figures 1 and 2). The CM functions of the H_2CO product and related channels 5 and/or 6 are confirmed by measurements at the parent ion (m/z = 30) of H_2CO, which was observed together with some daughter ions of the H channel 1 (see Figure 2, top panel). The angular and TOF data (not shown here) at m/z = 56 and 55 gave clear indication of two H-elimination channels 1 and 2 and of the H_2 elimination channel 7, while the data at m/z = 15 gave unambiguous determination of channel 4 by detection of CH_3 and its coproduct CH_2CHO (vinoxy) (via its daughter ion CH_3^+).
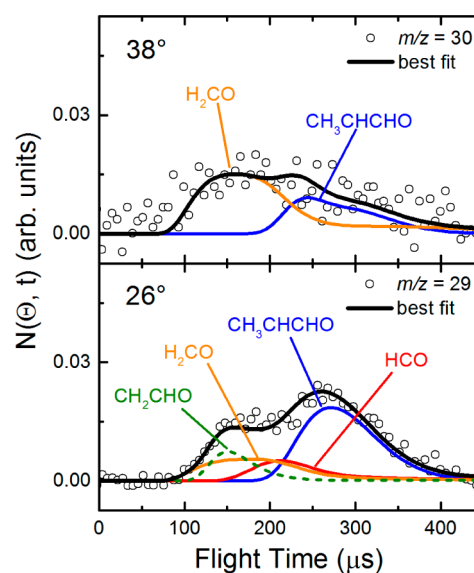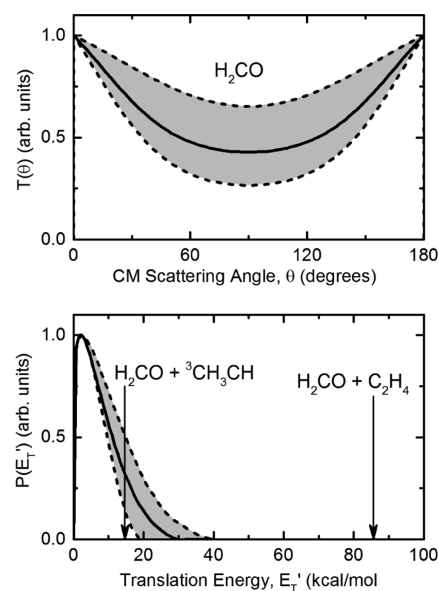

Figure 3. Best-fit CM angular (top) and translational energy (bottom) distributions for the $H_2CO + {}^3CH_3CH/C_2H_4$ channels. Arrows mark the total available energy (=$E_c − \Delta H^\circ_0$) for channels 5 and 6. Shaded areas indicate the limits of the error bars for the CM functions (see the text).

Shaded areas in Figure 3 delimit the range of $T(\theta)$ and $P(E'_T)$ functions that still produce a satisfactory fit of the LAB data. As can be seen the sensitivity of the experimental data to the degree of polarization of $T(\theta)$ is not very high as the size of the error bar area clearly witnesses because the H_2CO channel is only a fraction of the total angular distribution measured at m/z = 29. In contrast, sensitivity is higher for the product translational energy distribution. As can be seen in the bottom panel of Figure 3, the best-fit $P(E'_T)$ for the H_2CO forming channel(s) peaks at 2.4 kcal/mol and extends up to about 30 kcal/mol, with an average fraction of energy released in translation of 8.2 kcal/mol. Considering that the exoergicity of channel 6 is 5.4 kcal/mol, the best-fit $P(E'_T)$ extends (outside of the uncertainty of the error bars) somewhat beyond the limit of
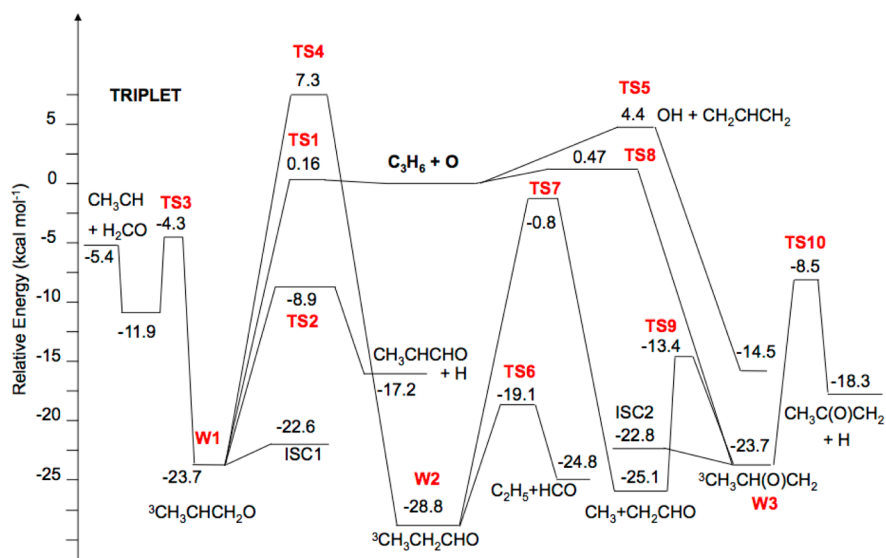
Figure 4. Potential energy diagram illustrating stationary points on the triplet C_3H_6O PESs. Structures and vibrational frequencies were computed at the CASPT/aug-cc-pVTZ level. Energies were computed at the CCSD(T)/CBS level, with exception for reactions with multireference character, in which case CASPT2 energies calculated with extended active spaces are reported (see the SI for details).

energy conservation for the triplet channel. This, together with the fact that the high-energy tail of the $P(E'_T)$'s never reaches the maximum value of the available energy when two molecular products are formed, might be taken as an indication that some H_2CO is also formed from the singlet PES, where the exoergicity of channel 5 is 76 kcal/mol. Unfortunately, the resolution of our experiment does not allow us to disentangle unambiguously the triplet and singlet relative contributions to formaldehyde formation.

The PES used in the study of the reactivity between $O(^3P)$ and propene was constructed following the same procedure of previous computational investigations of the singlet and triplet C_3H_6O PES[24,31] and of the C_2H_4O PES,[5,32,33] which were complemented by an additional search for new possible reaction channels. To understand this reactive system, one should address (i) the role of the two entrance channels, following the O atom attack either on the terminal or central C atom; (ii) the reactivity on the triplet PES; (iii) the ISC extent; and (iv) the reactivity on the singlet PES. The PES analysis has revealed that the main $^3CH_3CH + H_2CO$ reaction channel occurs on the triplet PES and that the considered singlet $H_2CO + C_2H_4$ channel plays a very minor role for this system. Other channels occurring on the triplet PES are 1, 2, and 4. In this work, we report computational results only for the channels of the triplet PES, with ISC treated as one of them. The triplet PES, which was computed combining CASPT2 and CCSD(T) electronic structure calculations as described in detail in the SI, is shown in Figure 4.

The main features of the triplet PES are the following. Oxygen atoms can directly react with propene to give addition to the two unsaturated carbon atoms and hydrogen abstraction from the methyl group. All reactions are characterized by well-defined transition states. In the case of addition, the two transition states are connected on the reactant side to the same precursor complex (van der Waals like) lying about 1.9 kcal/mol (not shown in Figure 4) below the reactants energy. The presence of a precursor state is indicative of the existence of two distinct transition states, an inner and an outer transition state. In the investigated conditions, the rate fluxes are

controlled by the inner transition state because of the lower density of states and the relative small energy difference with respect to the outer transition state, as found by Sabbah et al.[9] The approach used to locate the transition states of the addition reactions is similar to the one adopted by Sabbah et al.,[9] as described in detail in the SI. The energy barrier of H abstraction from the CH_3 group of propene is 4.4 kcal/mol. The high-pressure rate constants calculated for the addition and abstraction reactions interpolated between 300 and 2000 K, and the channel-specific rate constants for the triplet PES for channels 1, 2, 3, 6, and ISC are reported in Table S2 (see the SI) and compared in Figure 5 with literature experimental data.

As can be observed in Figure 5, there is good agreement between the calculated and experimental measurements of the total rate constant in the investigated temperature range. The addition of $O(^3P)$ to the terminal carbon atom is exothermic by 23.7 kcal/mol and leads to the formation of a CH_3CHCH_2O biradical species (W1) that can follow several reaction routes, H transfer to the central carbon to form the triplet state of propanal (W2), H loss from the CH_2O group via TS2, decomposition to the CH_3CH biradical and H_2CO via TS3, and ISC (ISC1) to the singlet PES. Because of the high-energy barrier, (1,2)-H transfer leading to triplet propanal is not competitive with the other three processes in the investigated temperature range, so that its contribution to the overall system reactivity is negligible. The loss of atomic hydrogen from the initial triplet diradical (W1), $^3CH_3CHCH_2O$, can proceed through two distinct transition states with similar energy barriers (14.8 and 15.1 kcal/mol). It is a fast process and the main source of H atoms in the simulated conditions. Decomposition of CH_3CHCH_2O to $^3CH_3CH + H_2CO$ is the most important reaction route for the triplet PES because, though the computed energy barrier from the diradical intermediate is higher than that determined for the H loss channels (19.6 versus 14.8 kcal/mol), it has a high pre-exponential factor determined by the presence of two transitional modes with low vibrational frequencies (54.6 and 77.4 cm^{-1}) that were treated as hindered rotors. Following dissociation, a precursor complex is formed at an energy that is
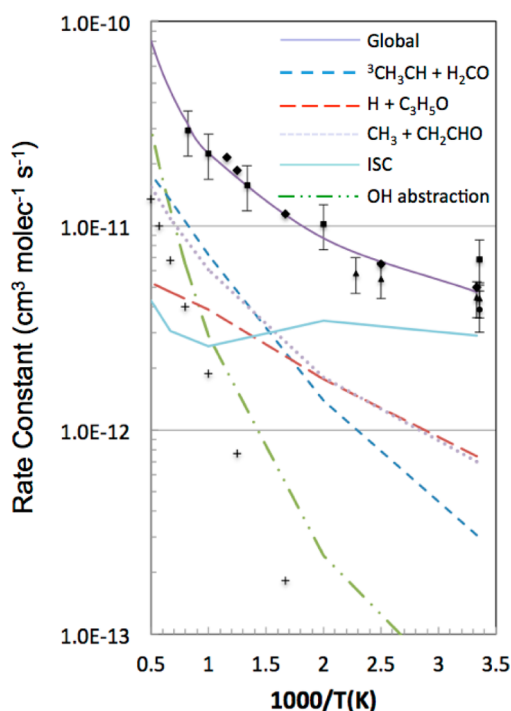
Figure 5. Comparison between the rate constants calculated for addition to the terminal and central C of propene for the $^3CH_3CH + H_2CO$, $CH_3 + CH_2CHO$, and $H + C_3H_5O$ channels and for H abstraction with experimental measurements of the global rate constants of ● Sabbah et al.,[9] ■ Mahmud and Fontijn,[10] ▲Atkinson and Pitts,[11] and ◆ Perry[12] and with the recommendation of Tsang[13] (+) for H abstraction to give the OH and CH_2CHCH_2 radicals.

about 6.5 kcal/mol lower than that of the decomposition products. The reactivity that follows O addition to the central C atom, which leads to the formation of W3 ($^3CH_3CH(O)CH_2$), is governed by the competition between decomposition to the methyl and vinoxy radicals via TS9, the loss of the hydrogen atom bound to the central C via TS10, and ISC (ISC2). The loss of CH_2 from W3 as well as H transfer to oxygen are not competitive with the other three processes because of the high-energy barriers. The energy barrier calculated for decomposition to methyl + vinoxy radicals is 10.4 kcal/mol (TS9), thus significantly smaller than that of H loss (15.2 kcal/mol, TS10), which makes the first process the dominant reaction route for this portion of the PES.

Master equation simulations were performed in the CMB conditions accounting explicitly for ISC, which was considered as an irreversible process. It was predicted that the $^3CH_3CH + H_2CO$ BR is 0.32, thus in reasonable agreement with the experimental value of 0.44 ± 0.15. Simulations were successively performed in a collisional environment at pressures of 0.1, 1, and 10 bar and temperatures between 300 and 2000 K. The calculated rate constant for the $^3CH_3CH + H_2CO$ channel, which is essentially pressure-independent, is shown in Figure 5, where it is compared with the total high-pressure rate constant, while Arrhenius parameters are reported in the SI. The simulations predict that the BR for this reaction channel grows from 0.06 to 0.16 between 300 and 500 K until it reaches a constant value of about 0.3 and becomes dominant above 1000 K.

The analogous channel for the $O(^3P) + C_2H_4$ reaction, leading to $^3CH_2$ and H_2CO, was also found to be of increasing importance with increasing E_c. The BR reaches a value of 0.20

$\pm$ 0.05 at the comparable E_c of 8.4 kcal/mol.[5,6] Nevertheless, the shapes of the best-fit $P(E'_T)$'s are very different as they mirror the rather different characteristics of the exit barriers for the two systems.

In conclusion, the present work shows that extrapolating room-temperature BRs to combustion temperatures may lead to considerable errors as new reaction channels may be activated with the increase of the available energy to the reacting system. For the system under study, it has been found that the $^3CH_3CH + H_2CO$ channel, which is almost negligible at room temperature (6%), becomes dominant at combustion temperatures (30−35%). It should be noted that the statistical BRs at 300 K are found to be in good agreement with the relative yields of the CH_3, C_2H_5, and H_2 channels determined in the kinetics work at 300 K of Savee et al.[20] but are not in agreement with the absolute BR of the H channel derived by Knyazev et al.,[19] which appears strongly overestimated. The details of these comparisons will be reported in a forthcoming full paper.

The $^3CH_3CH + H_2CO$ channel is a reaction route that is in general not included in combustion kinetics models[13,21−23] and that may have the potential to affect significantly the system reactivity as at combustion temperatures, $^3CH_3CH$ can easily isomerize to triplet ethylene, which may then undergo ISC to singlet ethylene, thus providing a termination route for the radical mechanism. If this were not the case, $^3CH_3CH$ and triplet ethylene would have the potential to react further along reaction routes that have presently not yet been explored. More importantly, as propene is a prototype species for all terminal alkenes, it is possible that the same reaction route may be active in the combustion of a large number of terminal alkenes. Therefore, we propose a generalized scheme for a new channel of this family of reactions

$$O(^3P) + R\text{-}CH{=}CH_2 \rightarrow R\text{-}CH + H_2CO$$
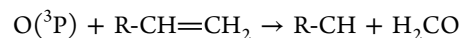
which should be significant under the high-energy/temperature conditions of combustion systems.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Details of the experiment, PES, and RRKM/ME calculations. This material is available free of charge via Internet.

AUTHOR INFORMATION
Corresponding Authors

*E-mail: carlo.cavallotti@polimi.it (C.C.).
*E-mail: piergiorgio.casavecchia@unipg.it (P.C.).
Present Addresses
§V.N.: Faculty of Safety Engineering, VŠB − Technical University of Ostrava, Ostrava, Czech Republic.
⊥A.B.: Institut des Sciences Moléculaires, Université de Bordeaux, UMR 5255 CNRS, 33400 Talence, France.
#S.F.: Dipartimento di Ingegneria Civile ed Ambientale, Università degli Studi di Perugia, 06125 Perugia, Italy.
Notes
The authors declare no competing financial interest.

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