

Product branching fractions for the reaction of O(³P) with ethene†

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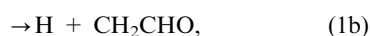
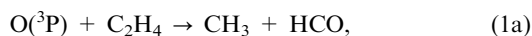
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The product branching fractions for the reaction of atomic oxygen with ethene, O(³P) + C₂H₄ → CH₃ + HCO (1a), → H + CH₂CHO (1b), → H₂ + CH₂CO (1c), have been investigated at room temperature (295 ± 4 K) and pressures from 1 to 4 Torr (with N₂ or He buffer) by a laser photolysis–photoionization mass spectrometry method. From the yield of CH₃ radical, φ(CH₃), the branching fraction for (1a) was determined to be 0.53 ± 0.04 and no apparent pressure dependence was found from 1.5 to 4.0 Torr (N₂ buffer). The ratio of the HCO yield to that of CH₃, φ(HCO)/φ(CH₃), was measured to be less than unity and increased as pressure increased (~0.7 at 1 Torr and ~0.9 at 4 Torr [He]) suggesting prompt dissociation of the hot HCO radical (to H + CO) formed by channel (1a) at low pressures. An interpretation which reduces the large discrepancy among branching fractions reported for low pressure region is presented. The existence of the molecular H₂-elimination channel (1c) was confirmed. The branching fraction for channel (1c) was determined to be 0.019 ± 0.001 by the yield of CH₂CO and was independent of pressure from 1.0 to 4.0 Torr (He buffer). As a side result, the yield of CH₃ radical from O(¹D) + C₂H₄ reaction was also determined.

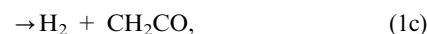
Introduction

The reactions of atomic oxygen with alkenes play an important role in the combustion of hydrocarbons as one of the dominant degradation processes of alkenes. Extensive kinetic measurements have revealed small, or even negative, activation energies,¹ suggesting that the reactions involve the initial electrophilic addition of atomic oxygen to the double bonds.² The product branching has been subject of various investigations for decades,^{3–20} and has been discussed in terms of the site preference of the initial oxygen-atom attack and the subsequent isomerization and/or dissociation processes of the biradical adducts.

As a reaction with the simplest and prototypical alkene, the reaction of ethene (C₂H₄) has been most extensively investigated. The rate constant has been measured experimentally from room temperature to 2300 K.⁵ After a long argument on the dominant channels,^{6–20} the reaction is now known to proceed *via* two major channels,



maybe with some contribution of minor channels,



Theoretical investigation also supported the initial formation of the triplet biradical.^{21,22} A schematic energy diagram for the reaction is shown in Fig. 1. Earlier theoretical investigation²³ was focused on the triplet dissociation route of the biradical and showed that the simple H-elimination to produce H + CH₂CHO (1b) proceeds without a barrier higher than the reactants, while a significantly high barrier was found for the hydrogen shift to produce CH₃CHO, which may further

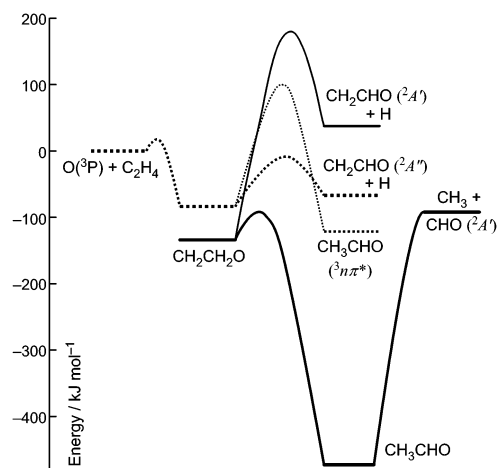


Fig. 1 Energy diagram for the O(³P) + C₂H₄ reaction based on the quantum chemical calculations.^{24,25} Dotted and solid lines denote triplet and singlet surfaces, respectively.

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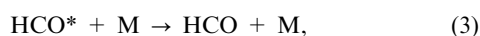
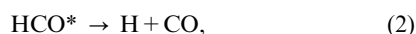
† Electronic supplementary information (ESI) available: Detailed experimental results for O(¹D) + C₂H₄ and for the determination of CH₂CO yields, as well as additional information on quantum chemical calculations. See DOI: 10.1039/b905787k

dissociate to $\text{CH}_3 + \text{HCO}$ (1a). Later theoretical investigations^{24,25} including singlet surfaces supported the earlier calculation, and also indicated that, on the singlet surface, a hydrogen shift to CH_3CHO proceeds easily while an H-elimination process involves a significantly high barrier.

The theoretical investigations suggest two major product channels, namely, direct dissociation of the triplet biradical to $\text{H} + \text{CH}_2\text{CHO}$ (1b) and a process involving ISC (intersystem crossing) to singlet biradical followed by the hydrogen-shift isomerization to acetaldehyde and further by the C–C bond fission to $\text{CH}_3 + \text{HCO}$ (1a). One of the main questions of the experimental investigations in the last three decades was how the reaction involves the ISC, that is, whether the ISC is induced by collisions or not. The experimental studies in the early 1980s at moderate pressures⁸ (80–760 Torr) and collision-free molecular beam condition⁹ seemed to be consistent with the collision induced ISC mechanism, that is, the triplet channel (1b) dominates at collision free condition while both singlet (1a) and triplet (1b) channels are significant at higher pressures, although this interpretation contradicted an earlier qualitative measurement⁶ which had reported a significant formation of CH_3 and HCO even at the collision free condition.

However, a later low-pressure (30 mTorr) experiment¹² and revised molecular beam experiment¹⁵ showed significant branching to the singlet channel (1a) which involves ISC, suggesting the fast ISC without collisions. The argument seemed to be settled after the report¹⁶ which suggested the collision-induced ISC mainly from the pressure dependence of the yield of hydrogen atoms observed in the authors' and earlier measurements.^{10,11,14} More recently, two molecular beam experiments have been reported.^{18,20} The reported branching fractions for (1b) significantly differ from each other, $\phi_{1b} = 0.62$ (ref. 18) and 0.27 (ref. 20).

The discrepancy of ϕ_{1b} at lower pressures seems to be left unresolved since no crucial flaw could be found in either experimental investigations. However, an inspiring experimental information was reported by Quandt *et al.*,³ who observed a direct formation of CO molecule in the reaction of $\text{O}({}^3\text{P}) + \text{C}_2\text{H}_4$ under single collision conditions. Since the C–H bond dissociation energy of HCO ($D_{298}^\circ = 65.7 \text{ kJ mol}^{-1}$) is smaller than the exothermicity of channel (1a), $113.2 \text{ kJ mol}^{-1}$, the most probable source of the CO will be the dissociation of hot HCO formed *via* channel (1a), and they estimated that about half of H atoms are produced by the dissociation of HCO . Considering that the strong pressure dependence of ϕ_{1b} has been seen only in the measurement of H-atoms, the mechanism including the hot HCO (HCO^*) dissociation and the competing stabilization,



seems to explain the contradiction between H-atom measurements and others.

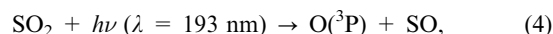
In the present study, the product yield from $\text{O}({}^3\text{P}) + \text{C}_2\text{H}_4$ has been reinvestigated since few measurements for product other than H-atom have been reported in the intermediate pressure range (0.1–100 Torr). In the pressure range from 1 to

4 Torr, the yields were determined for CH_3 and HCO for channel (1a), and CH_2CO for channel (1c).

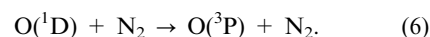
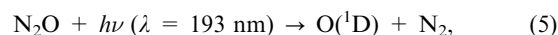
Experimental

Experiments were carried out on a laser photolysis–photoionization mass spectrometry apparatus. The apparatus is similar to those developed by Washida and co-workers.²⁶ In a tubular Pyrex glass reactor (15.6 mm id), flowing sample gas containing the precursor molecule for atom or radical was irradiated by pulsed 193-nm ArF excimer laser (Lambda Physik, COMPex 102) light. Gases were introduced to an ionization chamber through a pinhole (200 μm id) located at the side wall of the reactor. Reactant or product radicals were ionized by vacuum-ultraviolet light from a resonance lamp powered by microwave discharge. An H-lamp with MgF_2 window (10.20 eV, $2^2\text{P}_J - 1^2\text{S}_{1/2}$) was used for the ionization of CH_3 radical (ionization potential [IP] = 9.84 eV), CH_2CO (IP = 9.62 eV), and NO (IP = 9.26 eV), and Kr-lamp with CaF_2 window (10.03 eV, $5s^2[3/2]_1^0 - 4p^6\ 1\text{S}$) was used for CH_3 and HCO (IP = 8.14 eV). Ions were mass-selected by a quadrupole mass filter (Anelva, AQA-200) and detected by stacked multichannel plates. Pulsed ion signals were discriminated and counted by a multichannel scaling circuit interfaced to a microcomputer. The gas flow velocity was kept high enough to assure the gas replacement between laser shots (repetition rate: 4–9 Hz).

$\text{O}({}^3\text{P})$ atoms were generated either by 193-nm photolysis of SO_2 ,



or by 193-nm photolysis of N_2O followed by rapid quenching with N_2 ,



The initial O-atom concentration was kept low ($3\text{--}6 \times 10^{11} \text{ atoms cm}^{-3}$) to minimize the effect of subsequent radical–radical or radical–atom reactions. For the determination of CH_2CO yield, the initial O-atom concentration was determined by measuring NO formed by the reaction,



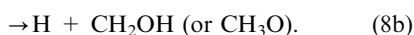
All experiments were performed at room temperature ($295 \pm 4 \text{ K}$). The error limits reported with the experimental results are two standard deviations throughout the paper. The gases used were obtained from Nippon Sanso (He, >99.9999%; N_2 , >99.9999%; SO_2/He standard gas, 4.97%; $\text{N}_2\text{O}/\text{He}$ standard gas, 9.98%, NO_2/He standard gas, 5.0%), Takachiho (C_2H_4 , >99.9%; CH_4 , >99%), ISOTEC ($^{13}\text{C}_2\text{H}_4$, >99% isotopic purity), and Katayama (CCl_4 , >99%; CH_3COCH_3 , >99%). Formaldehyde (H_2CO) was prepared by the thermal decomposition of paraformaldehyde²⁷ (Wako, >95%) and purified by trap-to-trap distillation. Ketene (CH_2CO) was prepared by the thermal decomposition of diketene (Tokyo Kasei, >99%).

Results

Branching fraction for (1a) [$\rightarrow\text{CH}_3 + \text{HCO}$]

The determination of the branching fractions for the major channels (1a) and (1b) might be influenced by the dissociation of HCO^* (2) when the yield of HCO or H atom was measured, as described above. Thus, in the present study, the branching fraction for channel (1a), ϕ_{1a} , was determined by measuring the CH_3 radical yield, $\phi(\text{CH}_3)$, against the initial O-atom concentration under the condition of excess C_2H_4 .

The CH_3 yield was determined by comparing CH_3 signal intensity with that from the reference reaction,



The $\text{O}(^1\text{D})$ atoms were generated by 193-nm photolysis of N_2O in He buffer. For the observation of $\text{O}(^3\text{P}) + \text{C}_2\text{H}_4$ products, $\text{O}(^1\text{D})$ was quenched by using N_2 buffer. The ratio of the CH_3 concentration observed in $\text{N}_2\text{O}/\text{C}_2\text{H}_4/\text{N}_2$ mixture to that in $\text{N}_2\text{O}/\text{CH}_4/\text{He}$ mixture, at the same N_2O concentration and laser fluence, gives ϕ_{1a}/ϕ_{8a} . The experiments with two gas mixtures were alternately repeated to cancel the error due to gradual change of the sensitivity, laser fluence, *etc.* The quenching of $\text{O}(^1\text{D})$ by He (rate constant $< 3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)²⁸ was negligible under the present experimental conditions.

Examples of the observed CH_3 signals are shown in Fig. 2. Since the detection sensitivity was significantly different under He and N_2 buffer, the signal intensities were corrected against this effect. The sensitivity difference was calibrated by separate experiments using the photolysis of acetone, $\text{CH}_3\text{COCH}_3 + h\nu$ ($\lambda = 193 \text{ nm}$) $\rightarrow 2 \text{ CH}_3 + \text{CO}$, in He and N_2 buffer. Though minor, some further corrections were also made against: (1) $\text{O}(^1\text{D})$ loss by $\text{O}(^1\text{D}) + \text{N}_2\text{O}$, (2) $\text{O}(^1\text{D})$ reaction with C_2H_4 , and (3) $\text{O}(^3\text{P})$ heterogeneous loss at the reactor wall. The rate constants used for the correction were taken from the literature.^{5,29,30} The CH_3 yield from $\text{O}(^1\text{D}) + \text{C}_2\text{H}_4$ reaction was derived to be 0.54 ± 0.03 , from a separate experiment. [See ESI† for details.] The heterogeneous loss rate of $\text{O}(^3\text{P})$ was also derived from a separate experiment.

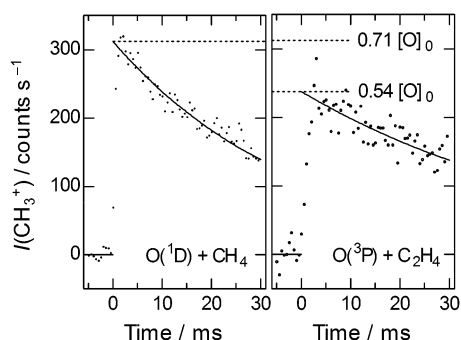


Fig. 2 Measurement of the yield of CH_3 radical from $\text{O}(^3\text{P}) + \text{C}_2\text{H}_4$. Left trace: CH_3 signal observed in the photolysis of $\text{N}_2\text{O}/\text{CH}_4/\text{He}$ mixture ($[\text{N}_2\text{O}] = 13.6 \text{ mTorr}$, $[\text{CH}_4] = 129 \text{ mTorr}$, total pressure = 4.0 Torr, ArF laser fluence = 8.6 mJ cm^{-2}). Right trace: CH_3 signal observed in the photolysis of $\text{N}_2\text{O}/\text{C}_2\text{H}_4/\text{N}_2$ mixture ($[\text{C}_2\text{H}_4] = 32.9 \text{ mTorr}$, Other conditions are the same as the left trace).

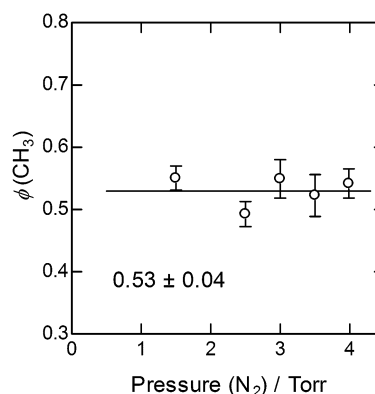


Fig. 3 Yield of CH_3 from $\text{O}(^3\text{P}) + \text{C}_2\text{H}_4$ reaction, $\phi(\text{CH}_3)$. Experimental conditions were similar to Fig. 2 except for the N_2 pressure.

The branching fraction for 8a, $\phi_{8a} = 0.71 \pm 0.05$, was taken from a recent direct measurement of OH radical yield³¹ using $\text{O}(^1\text{D}) + \text{H}_2 \rightarrow \text{OH} + \text{H}$ as a reference reaction. The CH_3 radical yield from $\text{O}(^3\text{P}) + \text{C}_2\text{H}_4$ was measured in the pressure range from 1.5 to 4.0 Torr (N_2), and the results are shown in Fig. 3. No apparent pressure dependence was found. As an average, the CH_3 yield, that is, the branching fraction for (1a) was determined to be $\phi_{1a} = 0.53 \pm 0.04$.

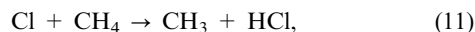
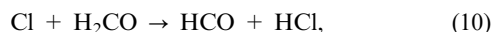
HCO Yield from $\text{O}(^3\text{P}) + \text{C}_2\text{H}_4$

In order to examine the possibility of the dissociation/stabilization mechanism, reactions (2) and (3), respectively, of hot HCO^* formed *via* channel (1a), the ratio of the yields of HCO to CH_3 , $\phi(\text{HCO})/\phi(\text{CH}_3)$ was measured as a function of the pressure (He buffer) in the present study.

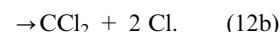
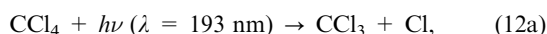
Since the HCO^+ signal at $m/z = 29$ overlapped with the C_2H_5^+ from ethyl radical formed by



carbon-13 ethene ($^{13}\text{C}_2\text{H}_4$) was used for this experiment. $\text{O}(^3\text{P})$ atoms were generated by 193-nm photolysis of SO_2 . The signals at $m/z = 30$ (H^{13}CO^+) and $m/z = 16$ ($^{13}\text{CH}_3^+$) were alternately recorded in the repeated experiments. In order to minimize the possibility of interference from fragment ions, a Kr-lamp with CaF_2 window, which has the lowest photon energy sufficient to ionize both CH_3 and HCO, was used. Sensitivity difference between HCO and CH_3 was calibrated by a separate experiment, using



where Cl atoms were generated by the 193-nm photolysis of CCl_4 ,



From the alternately repeated experiments observing HCO in the $\text{CCl}_4/\text{H}_2\text{CO}/\text{He}$ mixture and observing CH_3 in $\text{CCl}_4/\text{CH}_4/\text{He}$, the sensitivity ratio was determined to be $S(\text{HCO})/S(\text{CH}_3) = 0.63 \pm 0.07$ for the Kr lamp. To minimize the influence of the heterogeneous loss of Cl atoms, the concentration of H_2CO or

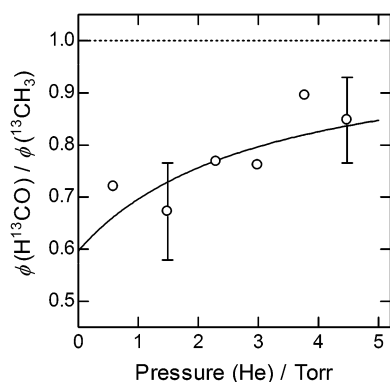


Fig. 4 Ratio of the yield of H^{13}CO to that of $^{13}\text{CH}_3$ from $\text{O}(^3\text{P}) + ^{13}\text{C}_2\text{H}_4$ reaction measured by 193-nm photolysis of $\text{SO}_2/\text{C}_2\text{H}_4/\text{He}$ mixtures. Experimental conditions: $[\text{C}_2\text{H}_4] = 28$ mTorr, $[\text{SO}_2] = 6.2$ mTorr, laser fluence = 0.5 mJ cm^{-2} .

CH_4 was chosen so that the time constant for reaction (10) or (11) is less than 0.2 ms. Since reaction (11) is slow and high concentration of CH_4 was required, a correction was made against the sensitivity change due to the large amount of CH_4 (probably caused by the VUV absorption of CH_4 in the ionization chamber) by a separate calibration experiment.

The yield ratio, $\phi(\text{HCO})/\phi(\text{CH}_3)$, was determined in the pressure range 0.6–4.5 Torr (He buffer), and is shown in Fig. 4. The determined ratio was less than unity and pressure-dependent. The observed behavior is consistent with the dissociation/stabilization mechanism of hot HCO^* radical. By assuming a simple Lindemann–Hinshelwood type mechanism for reactions (2) and (3), the yield ratio can be expressed as

$$\frac{\phi(\text{HCO})}{\phi(\text{CH}_3)} = \phi_0 + (1 - \phi_0) \frac{[\text{M}]}{(k_2/k_3) + [\text{M}]} \quad (13)$$

where ϕ_0 is the yield ratio at zero-pressure, that is, the fraction of HCO which survives even at zero-pressure. Here, k_2 and k_3 denote the rate constants for reactions (2) and (3), respectively, and $[\text{M}]$ is the concentration of buffer gas. The solid line in Fig. 4 shows a least-squares fit to eqn (13). The parameters in eqn (13) were derived to be $\phi_0 = 0.60$ and $k_2/k_3 = 1.0 \times 10^{17} \text{ molecule cm}^{-3}$ ($= 3.0$ Torr).

Branching fraction for (1c) [$\rightarrow \text{H}_2 + \text{CH}_2\text{CO}$]

Since few branching-fraction measurements^{7,19} have been reported for this channel so far, experimental determination was done by measuring the yield of CH_2CO . The initial concentration of $\text{O}(^3\text{P})$ was measured by observing NO from the reaction of $\text{O}(^3\text{P})$ with NO_2 (7). Since the subsequent reaction of CH_2CHO [formed *via* the channel (1b)] with other radicals,



where $\text{X} = \text{O}(^3\text{P}), \text{CH}_3, \text{etc.}$, may produce CH_2CO as well, the experimental conditions were carefully chosen to avoid the subsequent reactions. The signal intensity of CH_2CO linearly depended on the initial concentration of $\text{O}(^3\text{P})$ at lower concentration while it significantly curved at higher concentration above $\sim 10^{12} \text{ atoms cm}^{-3}$. The initial concentration was kept low enough, $\sim 3 \times 10^{11} \text{ atoms cm}^{-3}$. Further, the

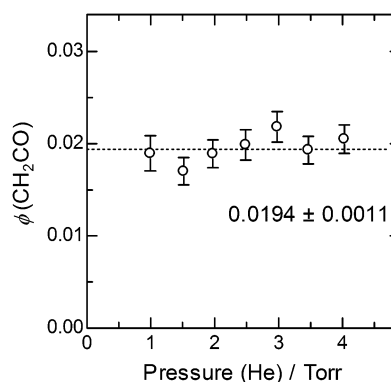


Fig. 5 The yield of ketene from $\text{O}(^3\text{P}) + \text{C}_2\text{H}_4$ reaction, $\phi(\text{CH}_2\text{CO})$, measured by 193-nm photolysis of $\text{SO}_2/\text{C}_2\text{H}_4/\text{He}$ mixtures in comparison with $\text{SO}_2/\text{NO}_2/\text{He}$ mixtures. Experimental conditions: $[\text{C}_2\text{H}_4] = 20$ mTorr, $[\text{NO}_2] = 1.4$ mTorr, $[\text{SO}_2] = 2$ mTorr, laser fluence = 1.0 mJ cm^{-2} .

analysis of the rise rate of CH_2CO by changing the concentration of C_2H_4 gave a rate constant for $\text{O}(^3\text{P}) + \text{C}_2\text{H}_4$ (1) as $7.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is in good agreement with the reported⁵ rate constant for reaction (1) (7.2×10^{-13} at 295 K), which also supports the fact that the observed CH_2CO is the primary product of reaction (1). Details of these confirmation experimental results are shown in the ESI.†

Experiments of CH_2CO measurements in the photolysis of $\text{SO}_2/\text{C}_2\text{H}_4/\text{He}$ mixtures and NO measurements in the photolysis of $\text{SO}_2/\text{NO}_2/\text{He}$ mixtures were repeated alternately to obtain the signal intensity ratio of CH_2CO to NO. The ratio of the sensitivity of CH_2CO to that of NO, $S(\text{CH}_2\text{CO})/S(\text{NO})$ was determined by a calibration experiment as 22.6 ± 1.5 for H-lamp. The signal intensity ratios were thus converted to the concentration ratios and are plotted in Fig. 5. No apparent pressure dependence was found in the pressure range 1.0 to 4.0 Torr. The branching fraction for the channel (1c) was determined to be $\phi_{1c} = 0.019 \pm 0.001$, which is in reasonable agreement with the recent theoretical prediction, 0.024.²⁵

Discussion

In the present study, the branching fractions for channels (1a) and (1c) were determined as; $\phi_{1a} (\rightarrow \text{CH}_3 + \text{HCO}) = 0.53 \pm 0.04$ and $\phi_{1c} (\rightarrow \text{H}_2 + \text{CH}_2\text{CO}) = 0.019 \pm 0.001$, and no apparent pressure dependence was found in the pressure range 1–4 Torr (N_2 or He) in either channel.

HCO from reaction (1)

The yield of HCO from $\text{O}(^3\text{P}) + \text{C}_2\text{H}_4$ reaction, $\phi(\text{HCO})$, derived from the present results is plotted in Fig. 6 with the previous reports. Although not mentioned in the report, the HCO yield determined by LMR¹⁴ also showed pressure dependence and was in good agreement with the present result. Also the $\phi(\text{HCO})$ measured at higher pressure by visible absorption⁸ is in reasonable agreement with the extrapolation of the present results. These also support the possibility of the prompt dissociation of HCO^* (2). By comparing the LIF intensity of CO and H against those observed for the reaction $\text{O}(^3\text{P}) + \text{C}_2\text{H}_2$, Quandt *et al.*³ estimated the yield ratio

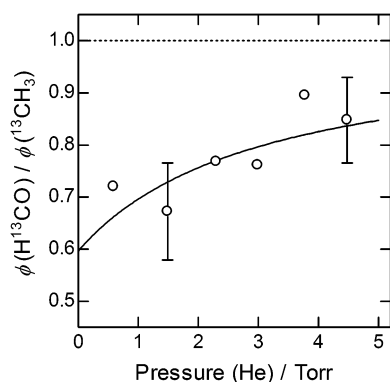


Fig. 6 Yields of HCO radical from $O(^3P) + C_2H_4$ reaction, $\phi(HCO)$. Closed circles (●) denote present results. Open triangles (Δ) and squares (□) denote previous measurements by LMR¹⁴ and visible absorption,⁸ respectively.

$\phi(CO)/\phi(H)$ to be ~ 0.5 at single collision conditions, which is in reasonable agreement with $\phi(CO)/\phi(H) = 0.35$ expected from the present measurement by extrapolation to the zero pressure by assuming $\phi_{1b} = 0.40$.²⁵

The vibrational structure of the HCO molecule has been well understood from recent spectroscopic³² and theoretical³³ studies. The vibrational state density is small at the low energy region of HCO. Only 15 vibrational states lie below the tunneling thresholds (=the H + CO asymptote), while 9 resonances were found between the classical threshold (the barrier height) and tunneling thresholds. It seems to be reasonable to expect that a significant portion of HCO is formed with the vibrational energies around the two thresholds, though a further quantitative argument requires detailed information on the energy distribution and collisional vibrational energy transfer processes, which is, however, unavailable. From the result of a simple analysis by eqn (13) ($k_2/k_3 = 1.0 \times 10^{17}$ molecule cm^{-3}) with the estimated collision rate, $k_3 \sim 4 \times 10^{-10}$ cm^3 molecule⁻¹ s⁻¹, the rate of unimolecular dissociation of HCO* was estimated to be $k_2 \sim 4 \times 10^7$ s⁻¹, which is in the allowable range for the resonances calculated³³ in the tunneling region [$< 2 \times 10^7$ for (0,1,3) and (0,0,5), 1.6×10^8 for (1,1,1), 3×10^9 for (1,0,3), and 2×10^7 for (0,3,0)].

Ketene channel: $\rightarrow H_2 + CH_2CO$ (1c)

In the present study, precise kinetic measurements of the ketene (CH_2CO) indicated that it is a primary product of the reaction of $O(^3P) + C_2H_4$. Since the product pair can only correlate the singlet potential energy surface, the molecular H_2 elimination most likely occurs on the singlet surface. Although

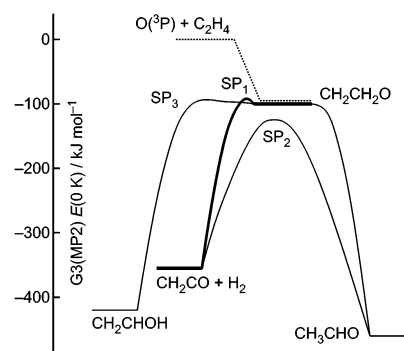


Fig. 7 Part of the energy diagram for $O(^3P) + C_2H_4$ system relevant to CH_2CO formation calculated by G3(MP2) method. The plotted energies are the potential energy corrected for the zero point energy. Dotted and solid lines denote triplet and singlet surfaces, respectively.

the major routes to $H_2 + CH_2CO$ have been characterized by Nguyen *et al.*,²⁵ direct 1,1- H_2 elimination from the singlet biradical suggested in a previous work¹⁵ has not been calculated.

Therefore, the direct 1,1- H_2 elimination transition state was searched by quantum chemical calculations by using Gaussian 98.³⁴ The results are shown in Fig. 7, and additional details are shown in the ESI.† The energies of the stationary points were estimated by G3(MP2) method.³⁵ It should be noted that the UHF calculations of the singlet biradical and the correlated transition states indicated a large spin contamination, $\langle S^2 \rangle = 0.5 \sim 1.0$, and the energy calculated by the UHF-based method might not be accurate enough.

The zero-point energy corrected G3(MP2) energy of the singlet biradical lies 99 $kJ mol^{-1}$ below the reactants, $O(^3P) + C_2H_4$, and 2 $kJ mol^{-1}$ below the triplet biradical. A saddle point, SP_1 , correlating the singlet biradical and $H_2 + CH_2CO$ was found at the energy only 7 $kJ mol^{-1}$ above the singlet biradical. Other features were essentially similar to the previous theoretical calculation.²⁵ Though Nguyen *et al.*,²⁵ predicted the branching fraction for $H_2 + CH_2CO$ (1c) to be 2.4% at 298 K as a sum of other three indirect channels, the direct elimination *via* SP_1 may be of some importance. The lack of apparent pressure dependence in the CH_2CO yield, $\phi(CH_2CO)$, suggests that the ISC is fast enough even in the present experimental pressure range (1–4 Torr).

Pressure dependence of the branching fraction and other channels

The present experimental results indicate no apparent pressure dependence of the branching fraction for (1a) or (1c). The

Table 1 Summary of the branching fractions for $O(^3P) + C_2H_4$

Channel	Present study (295 ± 4 K)	Theoretical ^a (298 K)	Evaluation ^b (298 K)
(1a) $CH_3 + CHO$	0.53 ± 0.04	0.477	0.6 ± 0.1
(1b) $H + CH_2CHO$		0.401	0.35 ± 0.05
(1c) $H_2 + CH_2CO$	0.019 ± 0.001	0.024	0.05 ± 0.1
(1d) $CH_2 + H_2CO$		0.052	
(1e) $CH_3CO + H$		0.022	
(1f) $CH_4 + CO$		0.023	

^a Ref. 25. ^b Ref. 5.

pressure dependence of HCO yield suggests prompt dissociation of HCO* formed *via* (1a). This implies that, at least some portion of the H-atom yield, which is observed to increase toward lower pressure, can be attributed to the result of HCO* dissociation. This interpretation seems to reduce the large discrepancy among the reported branching fractions at low pressures. However, the larger branching fraction for (1b) in a molecular beam experiment¹⁸ (0.62) as well as the smaller value (0.36) at moderate pressures⁸ (80 and 760 Torr) may still imply some pressure dependence in a wide pressure range. It seems to be obvious that ISC occurs without collision, though this does not contradict the possibility of further ISC enhancement by collisions.

In summary, the branching fractions determined in the present study are compared with the results of the theoretical investigation²⁵ and the evaluation⁵ in Table 1. Though not measured in the present study, reaction (1d) producing CH₂ + H₂CO has been recognized as one of the major channels.^{20,25}

Conclusions

(1) The branching fractions for O(³P) + C₂H₄ → CH₃ + HCO (1a) and → H₂ + CH₂CO (1c) have been determined to be 0.53 ± 0.04 [1.5–4.0 Torr (N₂)] and 0.019 ± 0.001 [1.0–4.0 Torr (He)], respectively, at room temperature. No apparent pressure dependence was observed in either branching fraction in the experimental pressure range.

(2) The yield ratio, $\phi(\text{HCO})/\phi(\text{CH}_3)$, was less than unity and pressure dependent, in agreement with a previous HCO measurement. This result, together with the reported direct CO formation, indicates the dissociation of hot HCO* (→H + CO) formed in (1a). The pressure dependence of $\phi(\text{HCO})/\phi(\text{CH}_3)$ could be explained by the competition between dissociation and collisional stabilization. This interpretation seems to reduce the discrepancy among previous branching fractions at low pressures.

(3) Precise kinetic measurements indicated the existence of the molecular elimination channel, (1c) (→H₂ + CH₂CO).

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References

- R. J. Cvetanović, *J. Phys. Chem. Ref. Data*, 1987, **16**, 261.
- R. J. Cvetanović and D. L. Singleton, *Rev. Chem. Intermediates*, 1984, **5**, 183.
- R. Quandt, Z. Min, X. Wang and R. Bersohn, *J. Phys. Chem. A*, 1998, **102**, 6; Z. Min, T.-H. Wong, R. Quandt and R. Bersohn, *J. Phys. Chem. A*, 1999, **103**, 10451.
- N. Washida, S. Inomata and M. Furubayashi, *J. Phys. Chem. A*, 1998, **102**, 7924.
- D. L. Baulch, C. T. Bowman, C. J. Cobos, R. A. Cox, Th. Just, J. A. Kerr, M. J. Pilling, D. Stocker, J. Troe, W. Tsang, R. W. Walker and J. Warnatz, *J. Phys. Chem. Ref. Data*, 2005, **34**, 757, and references therein.

- J. R. Kanofsky and D. Gutman, *Chem. Phys. Lett.*, 1972, **15**, 236; J. R. Kanofsky, D. Lucas and D. Gutman, *Proc. Combust. Inst.*, 1972, **14**, 285.
- F. J. Pruss, Jr, I. R. Slagle and D. Gutman, *J. Phys. Chem.*, 1974, **78**, 663.
- H. E. Hunziker, H. Knepe and H. R. Wendt, *J. Photochem.*, 1981, **17**, 377.
- R. J. Buss, R. J. Baseman, G. He and Y. T. Lee, *J. Photochem.*, 1981, **17**, 389.
- U. C. Sridharan and F. Kaufman, *Chem. Phys. Lett.*, 1983, **102**, 45.
- J. F. Smalley, F. L. Nesbitt and R. B. Klemm, *J. Phys. Chem.*, 1986, **90**, 491.
- Y. Endo, S. Tsuchiya, C. Yamada, E. Hirota and S. Koda, *J. Chem. Phys.*, 1986, **85**, 4446; S. Koda, Y. Endo, S. Tsuchiya and E. Hirota, *J. Phys. Chem.*, 1991, **95**, 1241.
- S. Koda, Y. Endo, E. Hirota and S. Tsuchiya, *J. Phys. Chem.*, 1987, **91**, 5840.
- U. Bley, P. Dransfeld, B. Himme, M. Koch, F. Temps and H. Gg. Wagner, *Proc. Combust. Inst.*, 1988, **22**, 997.
- A. M. Schmoltner, P. M. Chu, R. J. Brudzynski and Y. T. Lee, *J. Chem. Phys.*, 1989, **91**, 6926.
- V. D. Knyazev, V. S. Arutyunov and V. I. Vedenev, *Int. J. Chem. Kinet.*, 1992, **24**, 545.
- C. Anastasi, M. G. Sanderson, P. Pagsberg and A. Sillesen, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 3625.
- M. L. Morton, D. E. Szpunar and L. J. Butler, *J. Chem. Phys.*, 2001, **115**, 204.
- J. Peeters and D. Maes, *Tenth International Symposium on Gas Kinetics*, University College of Swansea, July 1988, p. A31.
- P. Casavecchia, G. Capozza, E. Segoloni, F. Leonori, N. Baulucani and G. G. Volpi, *J. Phys. Chem. A*, 2005, **109**, 3527.
- K. Yamaguchi, Y. Yabushita, T. Fueno, S. Kato and K. Morokuma, *Chem. Phys. Lett.*, 1980, **70**, 27.
- M. Dupuis, J. J. Wendoloski, T. Takada and W. A. Lester, Jr, *J. Chem. Phys.*, 1982, **76**, 481.
- C. F. Melius, J. S. Binkley, M. L. Koszykowski, as cited in K. Mahmud, P. Marshall and A. Fontijn, *J. Phys. Chem.*, 1987, **91**, 1568.
- T. Fueno, Y. Takahara and K. Yamaguchi, *Chem. Phys. Lett.*, 1990, **167**, 291.
- T. L. Nguyen, L. Vereecken, X.-J. Hou, M. T. Nguyen and J. Peeters, *J. Phys. Chem. A*, 2005, **109**, 7489.
- M. Masaki, S. Tsunashima and N. Washida, *Chem. Phys. Lett.*, 1994, **218**, 523; A. Miyoshi, H. Matsui and N. Washida, *J. Phys. Chem.*, 1990, **94**, 3016.
- R. Spence and W. Wild, *J. Chem. Soc.*, 1935, 338.
- K. Schofield, *J. Photochem.*, 1978, **9**, 55.
- R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr, J. A. Kerr, M. J. Rossi and J. Troe, *J. Phys. Chem. Ref. Data*, 1997, **26**, 521.
- O. Kajimoto and T. Fueno, *Chem. Phys. Lett.*, 1979, **64**, 445.
- F. Ausfelder, H. Hippler and F. Striebel, *Z. Phys. Chem.*, 2000, **214**, 403.
- D. W. Neyer, X. Luo, I. Burak and P. L. Houston, *J. Chem. Phys.*, 1995, **102**, 1645; C. Stöck, X. Li, H.-M. Keller, R. Schinke and F. Temps, *J. Chem. Phys.*, 1997, **106**, 5333, and references therein.
- H.-M. Keller, H. Floethmann, A. J. Dobbyn, R. Schinke, H.-J. Werner, C. Bauer and P. Rosmus, *J. Chem. Phys.*, 1996, **105**, 4983.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, *GAUSSIAN 98 (Revision A.7)*, Gaussian Inc., Pittsburgh PA, 1998.
- L. A. Curtiss, P. C. Redfern, K. Raghavachari, V. Rassolov and J. A. Pople, *J. Chem. Phys.*, 1999, **110**, 4703.