

On the reaction of OH radicals with C2 hydrocarbons

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Abstract

The reaction of hydroxyl radicals with fuel components and combustion intermediates is one of the most important steps for fuel oxidation. These reactions constitute the primary consumption pathways for hydrocarbons at atmospheric and combustion conditions. Depending on the chemical structure and thermodynamic conditions, different chemical pathways are available for the reaction of OH with hydrocarbons. Primarily, OH may abstract an H atom directly or may undergo addition reaction forming a complex which may produce various bimolecular products. The knowledge of the branching fractions and competition of these channels is crucial to understand the combustion behaviour of practical fuels. In this work, we report experimental study on the reaction of two C₂ hydrocarbons, ethylene and acetylene, with OH radicals and combine it with our previous work on ethane to draw conclusions on the effect of C-C bond type on the competition between association and abstraction/bimolecular channels over a wide range of thermodynamic conditions. Experiments were carried out behind reflected shock waves over 800 – 1300 K and the reaction progress was monitored by probing OH radicals using UV laser absorption near 306 nm. To discern association channel from C-H bond breaking channels (direct H-abstraction and bimolecular channels), reaction of OH radicals was studied with ethylene, deuterated ethylene, acetylene and deuterated acetylene. We previously showed that ethane + OH reaction expectedly follows solely direct H-abstraction pathway. Here, we found that ethylene + OH reaction presents a competition between association, bimolecular channels and direct H-abstraction of the vinylic H atoms, where association pathway becomes negligible for $T > 700$ K. On the other hand, acetylene is found to react with OH mainly through the association channel which dominates till temperatures as high as 1050 K.

Keywords: Ethane; ethylene; acetylene; association; dissociation; H-abstraction hydroxyl radical.

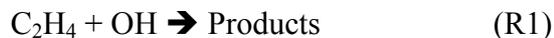
1. Introduction

The reactions of hydroxyl radicals with hydrocarbons are the most important consumption pathways at atmospheric and high-temperature combustion conditions. These reactions proceed *via* multiple channels due to different C-H sites and C-C bond types present in the molecular structure of various species [1]. Quantifying the competition between these channels is crucial in order to understand the oxidation characteristics of hydrocarbons. Even H-abstraction reactions may occur at different C-H sites with very different rates and eventually leading to very different subsequent chemistry. Westbrook et al. [2] reported a detailed analysis of the effect of molecular structure of hydrocarbons and oxygenates on their combustion behavior manifested by the research octane number (RON) and the octane sensitivity (OS). They concluded that the competition between H-abstraction and addition pathways is the primary factor for determining octane sensitivity. For example, alkanes are octane insensitive (i.e., have zero sensitivity) due to the unavailability of addition pathways [2]. Additionally, the allyl radical formed after H-abstraction from alkenes is much more stable than the alkyl radical formed after H-abstraction from alkanes [2]. Badra et al. [3] and Khaled et al. [4] studied the H-abstraction reaction of propene + OH and isobutene + OH and reported the branching ratios of the channels forming the resonantly stabilized allyl and 2-methyl-allyl radicals versus the more reactive propenyl and 2-methyl-1-propenyl radicals, respectively.

Direct experimental measurement of various channels of OH + fuel reaction is challenging since most experimental methodologies probe OH radicals as a measure of the rate of these reactions, and such techniques obscure individual contributions of various pathways [5, 6]. C₂ hydrocarbons are the building blocks for longer chain hydrocarbons and are among the most dominant intermediates produced during the oxidation of large hydrocarbons. Despite their simple structure, C₂ hydrocarbons represent an important case study to gain better understanding of the reactions with hydroxyl radicals. Ethane reactivity with combustion radicals has been studied extensively [7-9]. Although, the reaction of ethane (C₂H₆) with hydroxyl radicals solely undergoes direct H-abstraction [7, 9], the picture is very different for ethylene and acetylene due to the presence of double and triple C-C bonds, respectively.

Ethylene (C₂H₄) and acetylene (C₂H₂) reaction with hydroxyl radicals has been the focus of many theoretical and experimental studies; selected works are summarized in Table S1 (Supplementary Material) and further listings can be found in the NIST database [10]. Most of these studies concluded that the association of OH to C₂H₄ and C₂H₂ is the dominant pathway at temperatures less than 400 K and that direct H-abstraction and other bimolecular channels are dominant at high temperatures (T > 1000 K). At intermediate temperatures, however, the reactivity of ethylene and acetylene with OH radicals is still a gray area in literature and the competition between association, redissociation of the adduct, isomerization/decomposition of the adduct and direct H-abstraction channels is still unresolved.

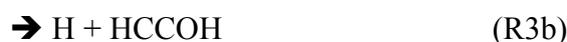
Liu et al. [11, 12] conducted a detailed experimental study of the reaction of ethylene and acetylene with OH radicals in a pulse photolysis cell between 333 and 1273 K at 1 atm. They employed deuteration to quantify the competition between H-abstraction and addition channels. They studied the following reactions:



For ethylene, Liu et al. [11] concluded that H-abstraction starts to dominate at temperatures higher than 650 K and that, at T < 500 K, ethylene reacts mainly through addition pathway leading to the stabilization of the alcohol adduct (see reaction R1e below). For acetylene, Liu et al. [12] supported the previous assertions of Smith et al. [13] that H-abstraction reaction prevails at temperatures higher than 1000 K. These experimental results were valuable inputs for the detailed theoretical works of Senosiain et al. [14, 15] who calculated various channels of the reaction of OH with ethylene and acetylene. The authors argued that vinyl alcohol (CH₂CHOH) is a non-negligible (~ 10%) product of the reaction of OH and ethylene even at temperatures higher than 800 K [14].



For acetylene, Senosiain et al. [15] estimated that the addition of OH to the triple bond followed by complex stabilization (R3f) or the formation of bimolecular products (R3b – R3e) are the main chemical routes of this system. They predicted that the rate coefficient for direct H abstraction (R1a) is relatively small and ketene (CH_2CO) is the primary product of this reaction at combustion-relevant conditions. However, they could not resolve discrepancies between their calculated total rate and the measurements of Liu et al. [12] at the intermediate-temperature region ($700 \text{ K} < T < 1200 \text{ K}$).



In this work, we aim to provide new high-temperature experimental data on the reaction rates of ethylene and acetylene behind reflected shock waves. We use the deuterated kinetic isotopic effect (DKIE) to differentiate between association (adduct stabilization) and other channels. We then compare our measured overall OH loss rates with previous experiments and theoretical calculations. Finally, we draw conclusions on the active pathways during the reaction of C2 hydrocarbons with OH at conditions ranging from atmospheric to combustion environments.

2. Experimental Methods

Reactions of ethylene (R1), deuterated ethylene (R2), acetylene (R3) and deuterated acetylene (R4) with hydroxyl radicals were studied behind reflected shock waves in the low-pressure shock tube (LPST) facility at King Abdullah University of Science and Technology (KAUST). The reaction rate coefficients were measured by monitoring the concentration of OH radicals using UV absorption spectroscopy at the well-characterized $R_1(5)$ transition of the A–X (0,0) electronic system of hydroxyl near 306.7 nm. The low-pressure shock tube facility, the UV laser setup and the experimental procedure have been described elsewhere [7]. Ethylene (99.9% purity) and acetylene (99.9%) were purchased from AH Gases. Deuterated compounds, C_2D_4 (99.9% D purity) and C_2D_2 (99.9% D purity) were obtained from CDN-Isotopes. Tert-butylhydroperoxide (TBHP, 70% solution in water) was purchased from Sigma Aldrich and used as a thermal source of OH radicals. TBHP is chosen as the OH precursor since it decomposes very rapidly (less than 10 μ s at $T > 800$ K; less than 1 μ s at $T > 1100$ K) to produce OH radicals [16]. High dilution in argon ($\sim 99\%$) was used to eliminate thermal effects, and high C2:TBHP ratios were used to follow pseudo-first-order kinetics. In order to model the measured OH time-histories, a kinetic mechanism was assembled which is comprised of TBHP chemistry from Pang et al. [17] and base chemistry from Zhou et al. [18] detailed isobutene model which contained C0-C2 AramcoMech reaction mechanism [19]. Kinetic simulations were performed in Chemkin-Pro while changing the C2:TBHP ratio and C2 concentration to identify conditions where OH decay is mainly sensitive to the target $C_2 + OH$ reaction. This analysis lead to the choice of mixture compositions used in experiments; see Table 1. Higher concentrations of acetylene and acetylene-D2 were needed because of their relatively slow reaction rate with OH radicals.

Table 1: Mixture compositions used in this work (balance Ar).

System	[Fuel]	[TBHP]
C_2H_4, C_2D_4	0.05-0.1%	20-70 ppm
C_2H_2, C_2D_2	1-2%	20-50ppm

Hydroxyl sensitivity plots for C_2H_4 and C_2H_2 at representative conditions of 1100 K and 1.5 atm are shown in Fig. 1S and 2S of the Supplementary Material. It is seen that OH decay is dominated by the $C_2 + OH$ reaction with minor interference from secondary reactions which mainly come from TBHP byproducts (CH_3 and acetone).

3. Results and Discussion

For hydrocarbon + OH reaction systems comprising of competing channels, comparison of experimentally measured ‘overall rates’ to theoretical rate coefficients is not a trivial exercise. This issue has been discussed by Senosiain et al. [15] and Es-sebbar et al. [20] in their respective works on acetylene + OH and propyne / allene + OH. Particularly, in specific conditions where association competes appreciably with redissociation or where thermodynamic equilibrium is reached at the time scale of the experiment, the overall loss rate of the OH radicals deviates from the total forward rate coefficient. Senosiain et al. [14] reported that at 700 K and 1 atm, the rates of association and back dissociation of reaction R1e are approximately equal. For acetylene, they predicted that such an equilibrium is reached at a higher temperature of ~ 810 K at 1 atm [15].

To account for the role of various OH channels, we calculated the overall OH loss rate from the theoretical work of Senosiain et al. [14, 15] at a pressure of 1.5 bar, temperatures of 300 – 2000 K, and mixtures of 1% acetylene / 50 ppm OH / Ar as well as 0.1% ethylene / 50 ppm OH / Ar. Homogeneous constant UV reactor Chemkin [21] simulations were performed using the assembled kinetic mechanism which contained reaction rates of ethylene + OH and acetylene + OH from Senosiain et al. [14, 15]. The theoretical overall OH loss rate was obtained from the decay rate of the calculated OH time-histories up to the OH half-life. Results showed that all channels are unidirectional at our conditions (300 – 2000 K, 1.5 bar) except for reactions leading to the stabilized adduct (R1e and R3f) which partially back dissociate to reactants at intermediate temperatures. The experimental overall OH loss rates were obtained in an analogous manner by fitting the experimental OH decay profiles with the assembled kinetic mechanism. The mechanism-fitting method was preferred over exponential

decay method due to the (minor) role of secondary reactions. Best-fit to the experimental profiles was obtained by varying the overall rate of the C2 + OH reaction.

Representative hydroxyl time-history profiles are presented in Fig. 1 for the four C2 molecules studied in this work (R1 – R4). Also shown are the best-fit profiles from the assembled kinetic mechanism and perturbations of $\pm 30\%$ from the best-fit rate. These perturbations clearly show that the OH decay is sensitive to the overall C2 + OH reaction.

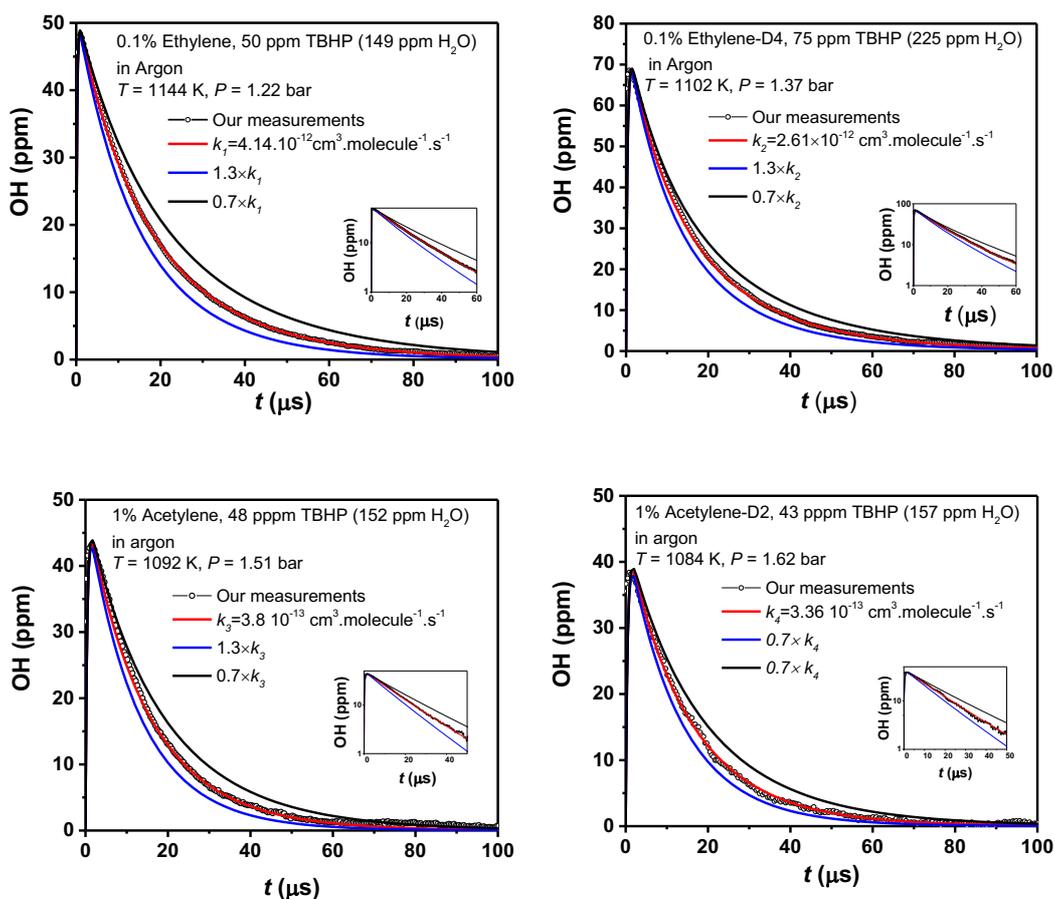


Figure 1: Experimental hydroxyl mole fraction profiles. Simulated best-fit (red solid line) and $\pm 30\%$ perturbations to the total rate of respective reactions (R1 – R4) are also shown. The insets plot OH mole fraction on a logarithmic scale.

Experimental results for the overall rate coefficients of reactions R1 – R4 are plotted in Fig. 2, and summarized in Tables S2 – S5 (Supplementary Material). Arrhenius expressions of the best-fit lines in Fig. 2 are given in Table S6 (Supplementary Material). Uncertainties in the reported rate coefficients of reactions R1 – R4 are estimated to be $\pm 12\%$ for ethylene (and acetylene-D4) and $\pm 14\%$ for acetylene

(and acetylene-D4). The uncertainties primarily come from the uncertainties in the fitting procedure ($\pm 5\%$), rates of secondary chemistry ($\pm 3\%$) and the reactant concentrations ($\pm 5\%$).

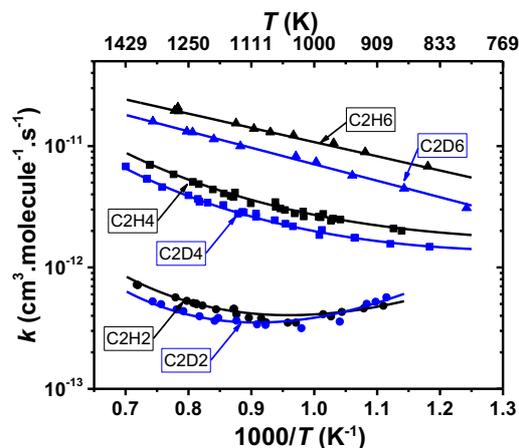


Figure 2: Reaction rate coefficients of C2 hydrocarbons with hydroxyl radicals. Ethane and deuterated ethane data are taken from [7]. Ethylene and acetylene data are from the current work. Solid lines represent 3-parameter Arrhenius best-fit to the measured rate coefficients (see Table S6).

Figure 2 also plots our previous measurements of the reaction rate coefficients of ethane (and ethane-D6) with hydroxyl radicals [7]:



Experimental rate measurements of C2 hydrocarbons with hydroxyl radicals show that ethane is more reactive than ethylene followed by acetylene. The slow reactivity of ethylene and acetylene can partly be explained by the decreased number of available H atoms for abstraction, and the corresponding energy barriers, 4.9 kcal/mol [14] for ethylene and 18 kcal/mol for acetylene [15], respectively, for abstraction reactions being higher compared to ethane + OH reaction (2.2 kcal/mol [7]). More importantly, at higher temperatures, even if the reactions of ethylene and acetylene with OH predominantly undergo *via* the formation of addition complex as opposed to direct H-abstraction, no significant amount of addition complex gets pressure stabilized and it will either dissociate back or isomerize and/or decompose to other bimolecular products *via* distinct barriers resulting into slowing down of these reactions [14, 15]. As can be seen in Fig. 2, the reactions of ethane and ethylene with OH exhibited the normal deuterium kinetic isotopic effect, i.e., $k(\text{light}) > k(\text{heavy})$. Undoubtedly, the

kinetic isotopic effect displayed by $C_2H_6 + OH$ reaction is the consequence of critical energy change due to isotopic substitution (see the slopes in Fig. 2). Here, the reaction coordinate involves the vibration of altered frequency which leads to the primary isotopic effect because only direct H-abstraction reaction is possible for $C_2H_6 + OH$. As for $C_2H_4 + OH$, $k(\text{light})$ and $k(\text{heavy})$ roughly run parallel curving strongly upward in their Arrhenius plot (see Fig. 2). Such kinetic behavior reveals that i) more channels open up and contribute significantly at high temperatures that have distinct energy barriers, ii) the reaction displays a normal kinetic isotopic effect which might be originating from either critical energy effect where H/D atoms are actually involved in the reaction (e.g., R1a – R1d) or statistical-weight effect (due to the difference in the quantum states of light and heavy molecules and the transition states). Finally, $C_2H_2 + OH$ shows quite interesting kinetic behavior. In this case, addition channel dominates over the abstraction channel, and the competing channels are R3b – R3f [15]. The Arrhenius plots in Fig. 2 clearly hint towards channel switching going from low to high temperatures. While the reaction of $C_2H_2 + OH$ exhibited a normal kinetic isotopic effect at high temperatures, a small inverse kinetic isotopic effect, i.e., $k(\text{heavy}) > k(\text{light})$ is observed at the low temperature end of our study ($T < 950$ K). Here again, both the primary and the secondary statistical-weight isotope effects may have contributed to the observed kinetic isotopic effect. Our data appear to be close to the high-pressure limit. At the high-pressure limit, the effect of statistical-weight isotopic effect may be either normal or inverse, but the rate constant ratio, $k(\text{heavy})/k(\text{light})$, will be close to unity as displayed by our data.

In order to compare our measured data with literature experimental data and theoretical calculations, rate coefficients of the reactions of ethylene and ethylene-D4 with OH radicals are plotted in Fig. 3. Also shown is the total forward rate (black solid line) of ethylene + OH reaction from Senosiain et al. [14]. We have included the calculated overall OH loss rates while using the thermal data of reactants and products from AramcoMech [22] (dark yellow line) and from Senosiain et al. [14] (red line). It may be noted that Senosiain et al. [14] have treated various conformers of C_2H_4OH adduct in more depth compared to the implementation in AramcoMech. We observe in Fig. 3 that the overall loss rates

and the total forward reaction rates are similar at conditions where the addition complex is either stable ($T < 500$ K) or negligibly produced ($T > 1100$ K). The dashed black line represents the summed contribution from direct H-abstraction and bimolecular channels (R1a + R1b + R1c + R1d) from Senosiain et al. [14] at 1.5 bar and compares well with Tully et al. [23] experiments which were carried out at low pressures (~ 0.12 bar) to minimize the role of the association channel. Likewise, the dashed blue line represents summation of H-abstraction and bimolecular channels for the reaction of OH with C_2D_4 , and was obtained by dividing the black dashed line with a DKIE factor for C_2H_4 to fit our high temperature data and those of Tully et al. [23] for $C_2D_4 + OH$ (with association pathway contribution removed).

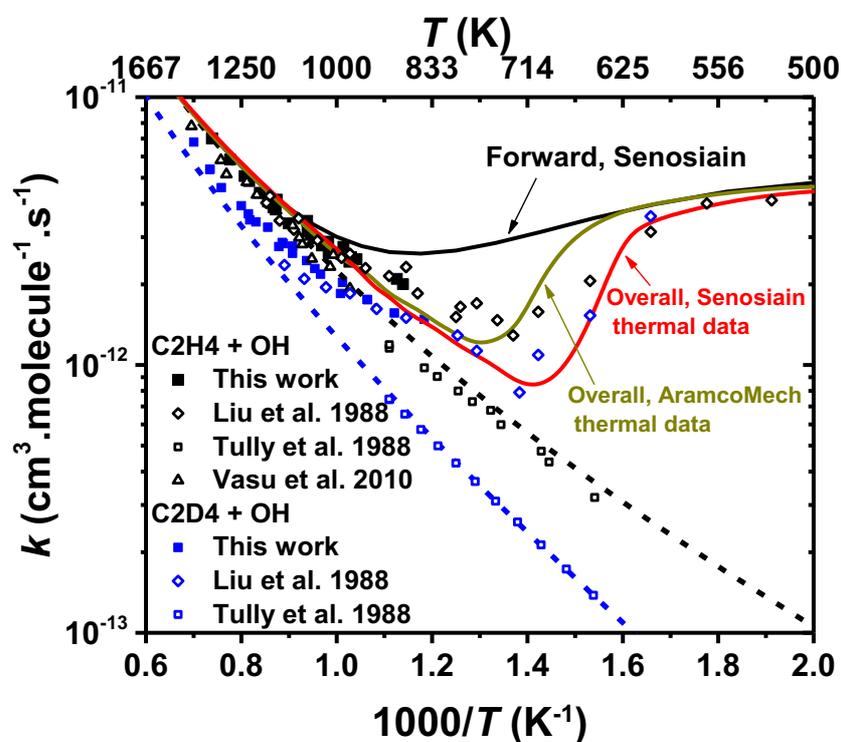


Figure 3: Rate coefficients of the reaction of ethylene and ethylene-D4 with OH radicals. Solid lines are calculations from Senosiain et al. [14]: Black line is the total forward rate coefficient of $C_2H_4 + OH$. Dark yellow and red lines are theoretical overall OH loss rates calculated using the AramcoMech thermal data and Senosiain thermal data, respectively. Dashed black line is Senosiain et al. [14] calculation for the bimolecular and the direct H-abstraction channels of $C_2H_4 + OH$. Dashed blue line is fit of our high T data and those of Tully et al. [23] for $C_2D_4 + OH$ with association pathway contribution removed.

Our measurements for the overall OH loss rate for $C_2H_4 + OH$ agree very well with those of Vasu et al. [24] and Liu et al. [11]. For $T < 1000$ K, overall loss rate calculations from Senosiain et al. [14]

(red line in Fig. 3) agree well with our measured hydroxyl overall loss rates. Small deviations between the measured and calculated overall loss rates are seen, which may arise due to the redissociation of the adduct which seems to be over-predicted by the calculations. The effect of thermo-chemistry is very important in this region as elaborated by comparing the thermal data of C_2H_4 , OH and C_2H_4OH from two different sources, namely AramcoMech [25] and Senosiain et al. [14]. Good agreement between Liu et al. [11] experiments and theory at low temperature (less than 600 K) indicates that the forward rate of the association channel is well captured by the theory since back dissociation and other channels are unimportant at these low temperatures. The calculated rates by Senosiain et al. [14] captured well our high temperature OH loss rates but these calculations did not accurately predict our data and those from Liu et al. [11] between 600 and 900 K. At this temperature range (600 – 900 K), the overall rate of the reaction is very sensitive to the thermodynamic parameters of the C_2H_4OH adduct.

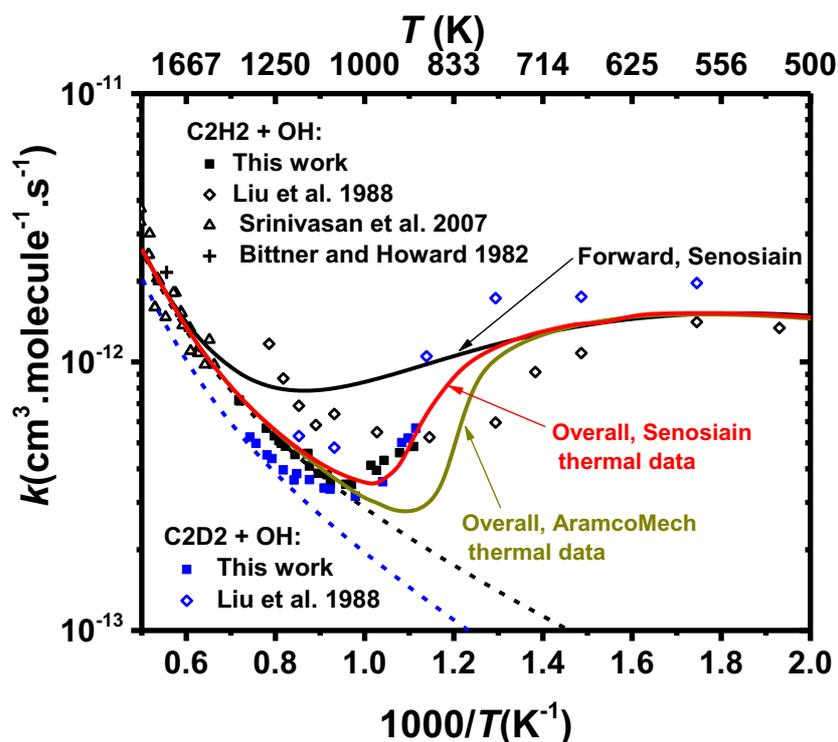


Figure 4: Rate coefficients of the reaction of acetylene and acetylene-D4 with OH radicals. Solid lines are the calculations from Senosiain et al. [15]: Black line is the total forward rate coefficient of $C_2H_2 + OH$. Red and dark yellow lines are theoretical overall loss rates calculated using the Senosiain thermal data and AramcoMech thermal data, respectively. Dashed black line is Senosiain et al. [15] calculation for the bimolecular and the direct H-abstraction channels of $C_2H_2 + OH$. Dashed blue line is fit of our high T data for $C_2D_2 + OH$ with association pathway contribution removed.

Rate measurements of acetylene + OH are compared in Fig. 4 with literature experimental data [12, 26, 27] and theoretical calculations [15]. Our high-temperature (1000 – 1393 K) measurements for $C_2H_2 + OH$ follow the trend of Srinivasan et al. [26] and Bittner and Howard [27] data obtained at $T > 1400$ K. However, Liu et al. [12] data are $\sim 60\%$ higher than our measurements at the high temperatures of their study. The same level of disagreement is seen between our measured rate coefficients of $C_2D_2 + OH$ and those of Liu et al. [12]. The discrepancy may be due to the temperature controlling system employed by Liu et al. [12]. The temperature was controlled at the outlet of the cell which could be different from that of the interior of the cell, particularly at high temperatures. Additionally, the high-temperature measurements of Liu et al. [12] may also be affected by the secondary chemistry. The overall loss rate calculations (red line) from Senosiain et al. [15] are in very good agreement with our measurements. The difference between the overall loss rate (red line) and the total forward rate (black line) over 700 – 1100 K is due to the back dissociation of the C_2H_4OH adduct. Similarly to the ethylene case, the inability of Senosiain et al. [15] calculation to accurately capture the data from Liu et al. [12] over 630 - 830 K suggests that improvement in the thermochemistry of the C_2H_2OH adduct may be needed.

Combining our studies on ethylene and acetylene reaction with hydroxyl radicals, we may argue that the association channel is an important pathway for the reaction of unsaturated C2 hydrocarbons with hydroxyl radicals. It seems that C_2H_2 preferentially reacts with OH through the addition pathway compared to C_2H_4 . The addition of OH to C_2H_2 plays a significant role at temperatures as high as 1050 K at $P \sim 1.5$ atm. On the other hand, addition of OH to C_2H_4 is a preferred pathway for temperature up to ~ 800 K. Beyond 800 K, direct H-abstraction and bimolecular channels becomes increasingly important for $C_2H_4 + OH$ reaction system. The analysis method presented here, together with our rate measurements and those from the literature, point to the importance of the thermochemistry of reaction adducts at intermediate temperatures.

4. Conclusions

In this work, we reported overall rate measurements of the reaction of C_2H_4 , C_2D_4 , C_2H_2 and C_2D_2 with OH radicals at high temperature (800 – 1400 K) and pressures near 1.5 bar behind the reflected shock wave. Overall loss rate measurements are compared to those of literature to draw comparative conclusions on the competition between association, direct H-abstraction and bi-molecular channels for C_2H_2+OH and C_2H_4+OH systems. The following are the main conclusions of this comparative study at $P \sim 1.5$ bar:

- Ethylene and acetylene react with OH through direct H-abstraction and adduct formation which can stabilize, redissociate or decompose to bimolecular products in contrast to ethane that reacts with OH only *via* H-abstraction.
- Ethylene + OH and acetylene + OH reactions mainly go through the association channel leading to the formation of corresponding stable adducts (C_2H_4OH and C_2H_2OH) for $T < 500$ K and $T < 700$ K, respectively.
- There is a strong competition between association, biomolecular product formation and direct H-abstraction channels between 500 – 850 K and 700 – 1050 K for ethylene and acetylene, respectively.
- The association adduct is not stable for $T > 850$ K (ethylene) or $T > 1050$ K (acetylene) and it totally redissociates to reactants. The ethylene + OH and acetylene + OH reactions then mainly go through direct H-abstraction and bimolecular channels.
- The stabilization (and equilibrium) of C_2H_4OH and C_2H_2OH adducts is mostly sensitive to their thermochemistry which has discrepancies in the literature, and hence merits further investigation in the light of the data and the analysis presented in this work.

Acknowledgements

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Table S1: Selected references for the work of C2 hydrocarbons with hydroxyl radicals. Units are, cm, s, K and molecule.

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Table S3: C₂D₄ + OH => Products rate coefficient measurements. Mixture: 0.1% C₂D₄/ 50-70 ppm TBHP /AR

Table S4: C₂H₂ + OH => Products rate coefficient measurements. Mixture: 1-2 % C₂H₂/ 20-50 ppm TBHP /AR

Table S5: C₂D₂ + OH => Products rate coefficient measurements. Mixture: 1% C₂D₂/ 20-50 ppm TBHP /AR

Table S6: Arrhenius Fitting parameters for the rate coefficients of C2 + OH => Products. Arrhenius function is: A.(T/1000)ⁿ.exp(-E/T). Used units are K, cm, molecule and s.

Figure S1. Hydroxyl sensitivity analysis for mixtures of ethylene at 1100 K and 1.5 atm. Mixture: 0.1% C₂H₄ + 50 ppm TBHP in argon. Hydroxyl sensitivity is defined as $S_{OH} = \left(\frac{\partial X_{OH}}{\partial k_i} \right) * \left(\frac{k_i}{X_{OH}} \right)$,

where X_{OH} is the local OH mole fraction and k_i is the rate coefficient for the ith reaction.

Figure S2. Hydroxyl sensitivity analysis for mixtures of acetylene at 1100 K and 1.5 atm. Mixture: 1% C₂H₂ + 50 ppm TBHP in argon. Hydroxyl sensitivity is defined as $S_{OH} = \left(\frac{\partial X_{OH}}{\partial k_i} \right) * \left(\frac{k_i}{X_{OH}} \right)$,

where X_{OH} is the local OH mole fraction and k_i is the rate coefficient for the ith reaction.

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