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Isomer-specific combustion chemistry in allene and propyne flames

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ABSTRACT

A combined experimental and modeling study is performed to clarify the isomer-specific combustion chemistry in flames fueled by the C_3H_4 isomers allene and propyne. To this end, mole fraction profiles of several flame species in stoichiometric allene (propyne)/O_2/Ar flames are analyzed by means of a chemical kinetic model. The premixed flames are stabilized on a flat-flame burner under a reduced pressure of 25 Torr (=33.3 mbar). Quantitative species profiles are determined by flame-sampling molecular-beam mass spectrometry, and the isomer-specific flame compositions are unraveled by employing photoionization with tunable vacuum-ultraviolet synchrotron radiation. The temperature profiles are measured by OH laser-induced fluorescence. Experimental and modeled mole fraction profiles of selected flame species are discussed with respect to the isomer-specific combustion chemistry in both flames. The emphasis is put on main reaction pathways of fuel consumption, of allene and propyne isomerization, and of isomer-specific formation of C_6 aromatic species. The present model includes the latest theoretical rate coefficients for reactions on a C_3H_5 potential [J.A. Miller, J.P. Senosiain, S.J. Klippenstein, Y. Georgievskii, J. Phys. Chem. A 112 (2008) 9429–9438] and for the propargyl recombination reactions [Y. Georgievskii, S.J. Klippenstein, J.A. Miller, Phys. Chem. Chem. Phys. 9 (2007) 4259–4268]. Larger peak mole fractions of propargyl, allyl, and benzene are observed in the allene flame than in the propyne flame. In these flames virtually all of the benzene is formed by the propargyl recombination reaction.

1. Introduction

Isomers are defined as chemical compounds with the same empirical formula but different bond structures. For instance, allene ($CH_2{=}C{=}CH_2$), characterized by two adjacent C=C double bonds, and propyne ($CH_3{-}C{\equiv}CH$), with one C-C single and one C≡C triple bond, are the two most stable C_3H_4 isomers. Because of such structural differences, isomeric compounds react differently under otherwise identical conditions. Isomer-resolving studies of flame compositions may yield improved kinetic models of combustion chemistry and an exceptionally detailed molecular-level description of molecular-weight growth processes. The present paper is a sequential article to Ref. [1], in which the isomer-resolved flame compositions of fuel-rich allene and propyne flames ($\phi = 1.8$) were compared with flame model predictions.

The isomer-specific differences in the compositions of flames fueled by allene and propyne are of particular importance for several reasons. First, allene and propyne constitute the smallest pair of structural isomers that allows for a detailed analysis of the influence of the chemical structure on the flame composition. Second, both allene and propyne are common combustion intermediates, and their reactions are critical in the formation of plausible precursors for aromatic species, including the resonantly stabilized propargyl (C_3H_3) and allyl (C_3H_5) radicals. Both radicals are critical elements of the gas-phase chemistry producing the “first aromatic ring” [2–8], i.e. phenyl and benzene, which then can react further to form polycyclic aromatic hydrocarbons (PAH’s) and ultimately soot [9]. Reaction of a propargyl radical with another propargyl is the dominant path to benzene/phenyl formation in many fuel-rich flames [4–6]. In flames fueled by allene and propyne, concentrations of propargyl and allyl radicals can build up to fairly high concentrations, so that the formation of the “first aromatic ring” in these flames should be clearly dominated by the corresponding $C_3 + C_3$ chemistry. Indeed, isomer-specific features of C_6H_6 formation in C_3H_4-fueled flames may provide rigorous tests of detailed combustion chemistry models describing the formation of aromatic hydrocarbons under combustion conditions.

Allene and propyne have been the subject of numerous experimental and theoretical studies that clarify the kinetics and

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mechanisms of various combustion-related reactions [1,10–29]. Special attention has been paid to the direct isomerization, which becomes feasible at high temperatures, and to the hydrogen-atom-assisted isomerization occurring on the C_3H_5 potential energy surface [30–32]. Previous low-pressure flame work includes studies of fuel-rich allene and propyne flames (Ref. [1]) and allene addition to various "base"-flames [19,23–25]. In our earlier study of the fuel-rich allene and propyne flames [1], the benzene formation was overpredicted by the combustion chemistry model by about a factor of 4. Because of this discrepancy, we find it necessary not just to refine the chemical kinetic mechanism, but also to provide additional experimental datasets from flames at a different stoichiometry. This broader set of four allene and propyne flames can now be used for the testing and development of chemical kinetic mechanisms.

In this work, isomer-resolving flame-sampling photoionization mass spectrometry and a chemical kinetic model, which has been improved since studying the isomeric compositions of fuel-rich allene and propyne flames [1], are used to unravel isomer-specific features in the combustion chemistry of stoichiometric premixed laminar low-pressure flames of allene and propyne. Very similar trends in temperature profiles and mole fraction profiles of the major species, including H_2, H_2O, CO, O_2, and CO_2 are found when allene or propyne are used as a fuel under otherwise identical conditions. However, clear differences between the flames are revealed for the relative formation of several intermediates, including but not limited to C_2, C_3, and C_6 species. The current chemical kinetic mechanism is capable of reproducing all experimental trends remarkably well. The present study highlights the critical features of the updated chemical mechanism, the isomer-specific differences between the two stoichiometric flames, and the formation pathways of the C_6H_6 isomers and their precursors in the stoichiometric and the previously reported fuel-rich flames [1].

2. Experiment

Premixed allene (propyne)/oxygen/44.4% argon flames with a fuel/oxygen equivalence ratio $\varphi = 1.0$ are stabilized on a flat-flame, stainless-steel McKenna burner at 25.0 Torr (=33.3 mbar) and a cold-flow reagent velocity of 43.2 cm/s at 298 K. Gases from those two low-pressure flames are sampled through a quartz probe of ~0.3 mm orifice, and a custom-built photoionization time-of-flight mass spectrometer is subsequently used to detect all combustion species simultaneously [33]. This instrument allows intermediates to be detected with concentrations as low as one part-per-million (1 ppm). Details of the fuel-rich ($\varphi = 1.8$) allene and propyne flames have been reported in Ref. [1]. Allene and propyne are purchased from Matheson Tri-Gas and their purities are given with >95% and 98%, respectively.

Isomer-specific detection and quantification of combustion intermediates are accomplished by using tunable synchrotron radiation at the Chemical Dynamics Beamline of the Advanced Light Source of the Lawrence Berkeley National Laboratory [5,33,34]. The photoionization mass spectrometer is configured to collect data in two modes. To resolve the isomeric composition of the combustion intermediates, the probe-to-burner distance is fixed and the photon energy is scanned to record so-called photoionization efficiency (PIE) spectra, which are photon-current normalized and integrated ion signals for a specific mass-to-charge (m/z) ratio [27–29,35–37]. In the second mode, the photon energy is fixed and the burner is scanned to produce mass spectra at each distance. Once the presence of different isomeric species has been established, the energy of the ionizing photons can be precisely tuned to minimize interferences caused by ionization of different isomers; i.e. ionization of the isomer with the larger ionization energy can be avoided. These data are subsequently analyzed to produce quantitative mole fraction vs. distance-from-burner profiles for comparison with models. More details of the flame-sampling photoionization mass spectrometer and the data analysis have been described elsewhere [38,39] and are not repeated here. We estimate the accuracy of the major species profiles to be within 20%. For other intermediates, especially the ones with unknown photoionization cross sections, the error can be as large as a factor of 4. The mole fraction profiles may be distorted by sampling probe perturbations [5]; this effect can especially be important close to the burner surface, where concentration gradients are the largest. However, the apparatus and data reduction procedures are the same for both flames; therefore, relative comparisons of mole fractions between flames have much smaller uncertainties.

Isomer-resolved mole fraction profiles of more than 40 flame species with masses ranging from 2 (H_2) to 94 (phenol) are determined for each flame. The entire dataset, which is available on request, shall not be presented in this paper. Instead we will highlight only the mole fraction profiles that are essential to understand the isomer-specific combustion chemistry of allene and propyne flames, including profiles of C_6H_6 isomers and its precursors.

Flame temperatures are measured with OH laser-induced fluorescence. The system is similar to that used in previous studies of McIlroy [40,41]. The visible output of a dye laser (Sirah Precision-Scan) is frequency-doubled at 50 Hz to produce light of ~306 nm, which is required to excite the OH A–X (0, 0) transition. The laser beam is focused with a 500-mm focal length lens at a distance of ~3 cm below the probe tip. The total fluorescence is monitored with a solar-blind photomultiplier tube with its gain set to produce a linear response over the expected range of signals. The accuracy of the measurements is estimated to be ±100 K in the postflame and reaction zone and somewhat larger in the preheat zone, where the OH concentrations are much smaller and the gradients much steeper. At the burner surface, a temperature of 500 K is assumed. The measured temperatures are represented as a smooth temperature profile that was taken as input for the model calculations. The larger uncertainty of the temperature profiles close to the burner surface ultimately reflects itself in a somewhat lower accuracy of the flame model predictions for this particular flame region, and probe perturbation in that region makes the lowest 1 mm unreliable for comparisons.

3. Modeling of the allene and propyne flames

The chemical kinetic model used in the present work is identical to the one used in our analysis of rich 1,3-butadiene flames [42]. It differs from the one we used previously in our study of rich allene and propyne flames [1] in a number of important ways. First, the present model reflects the recent theoretical analysis of reactions on a C_3H_5 potential by Miller et al. [30]. The most important reactions are

$$C_3H_4(a) + H \rightleftarrows C_3H_3 + H_2, \tag{R1}$$

$$C_3H_4(p) + H \rightleftarrows C_3H_3 + H_2, \tag{R2}$$

$$C_3H_4(a) + H(+M) \rightleftarrows C_3H_5(+M), \tag{R3}$$

$$C_3H_4(p) + H \rightleftarrows C_2H_2 + CH_3, \tag{R4}$$

$$\text{and } C_3H_4(a) + H \rightleftarrows C_3H_4(p) + H. \tag{R5}$$

In these reactions $C_3H_4(a)$ is allene, $C_3H_4(p)$ is propyne, C_3H_5 is allyl, and C_3H_3 is propargyl. These reactions play a dominant role in both rich and stoichiometric flames of both fuels.

The second key feature of the present model is our treatment of the propargyl recombination reaction. The rate coefficients and product distribution used here are based on the contracted model of the reaction introduced by Miller and Klippenstein [2], modified