



Hydrogen abstraction ratios: A systematic iPEPICO spectroscopic investigation in laminar flames

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ABSTRACT

The radicals produced by hydrogen abstraction in the initial fuel decomposition step are essential in combustion kinetics, but their experimental detection is very challenging. Imaging photoelectron photoion coincidence spectroscopy enables the detection and identification of even these isomeric radicals. Laminar low-pressure (40 mbar) hydrogen flames doped with different alkanes and alkenes are investigated systematically with the goal to identify the formation pathways and the fate of fuel radicals formed in hydrogen abstraction reactions. The abstraction reactions of primary, secondary, tertiary, and vinylic H atoms were never target of a systematic, direct semiquantitative investigation in a flame environment and this paper describes such a study for the first time. Performing the measurements at the vacuum ultraviolet beamline located at the Swiss Light Source enables isomer-selective detection of reactive radical species by imaging photoelectron photoion coincidence spectroscopy. For unambiguous identification of several isomeric radicals, threshold photoelectron spectra were compared with reference photoelectron spectra. H-abstraction ratios of isomeric radicals were determined and compared to literature reaction barriers and rate coefficients. In addition to the quantitative information, the peak positions of the profiles of radicals formed by hydrogen abstraction or addition to the fuel molecules as function of distance from the burner show faster H-abstraction for unbranched alkanes and alkenes than for branched fuels and faster H-addition than H-abstraction, respectively.

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1. Introduction

A key reaction most decomposition processes in pyrolysis as well as in combustion of hydrocarbons is the abstraction of a H atom (referred to as H-abstraction) by small radicals like O, OH, and H forming a radical (i.e., fuel radicals in the following). In particular, the initial fuel destruction steps in laminar low-pressure flames are dominated by these H-abstraction reactions [1] and are important for ignition processes [2–4]. Because the following reaction steps are highly dependent on the type of the formed radicals, the knowledge on H-abstraction pathways is essential for understanding and predicting combustion properties. The following reaction steps are dominated by oxygen addition, to form oxygenated species like alcohols, aldehydes, ethers etc., and further decomposition steps like abstraction of H atoms or hydrocarbons.

H-abstraction reactions of different hydrocarbons were the focus of several theoretical [5–10] and experimental studies [11–18]. Khaled et al. have investigated the reactions of linear alkenes [11] and *i*-butene [12] with OH radicals in shock tubes and showed that the reaction rate coefficients are dependent on the chain length and the position of the double bond, that is, the constitutional isomer. For example, the formation of the 2-methylallyl radical from *i*-butene is the dominating reaction channel. Zhou et al. presented in their study on *i*-butene [13] that the reactivity of the different abstraction reactants, such as H, O, OH, and CH₃ radicals, is mainly governed by the temperature. On the other hand, Li et al. investigated the oxidation process of 1-butene [14] by measuring ignition delay times and developed a chemical kinetic mechanism based on previous 2-butene [19] and *i*-butene [13] models. Zhang et al. used mass spectrometry [15] to investigate the pyrolysis of the butene isomers and found by reaction flux analysis that the decomposition of *i*-butene mainly proceeds through the 2-methylallyl radical via H-abstraction by small radicals. For the decomposition of 1-butene, fuel radicals formed

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by H-abstraction are not as relevant as the direct unimolecular scission of a CH_3 group in high-temperature environments [15]. Manion et al. [16] investigated H-abstraction reactions of *n*-alkanes by H and CH_3 radicals and showed a strong temperature dependence of the ratio between primary and secondary H-abstractions. The H-abstraction by CH_3 radicals from ethane was the target of the investigations by Möller et al. [17], while the decomposition of butane isomers by H radicals was investigated by Peukert et al. [18] in a shock tube study.

Complementary to the experimental studies, some theoretical investigations on H-abstractions are available. Extensive studies of these reactions at different alkane H sites were performed by Carstensen et al. [7] and Badra et al. [8]. A purely theoretical investigation on H-abstraction barriers of different alkanes by $\text{O}(^3\text{P})$ was published by Troya who came to the conclusion that the H-abstraction barrier in ($\text{O} +$ acyclic alkanes) reactions decreases in the following order: primary > secondary > tertiary, without being affected by the chain length [6]. Siddique et al. recently presented a theoretical study on the H-abstraction by amine radicals (NH_2) for a broad range of different hydrocarbons and obtained rate constants and standard enthalpies of activation [5].

While most of the experimental investigations on H-abstraction reactions in butanes and butenes were carried out using shock tubes [11–14,16–18,20–25], direct measurements of radical species in flame environments are still a challenging task. Schenk et al. [26], Dias et al. [27], and Oßwald et al. [28] reported molecular-beam mass spectrometric work on low-pressure, premixed, flat flames of the different butene and butane isomers. In situ flame-sampling mass spectrometric studies are one method of recording mole fraction profiles of several species in a flame environment, but the previous studies did not clearly identify isomeric compounds. Here, we present a detailed experimental study of H-abstraction reactions using the imaging photoelectron photoion coincidence spectroscopy (iPEPICO) endstation at the vacuum ultraviolet (VUV) beamline of the Swiss Light Source (SLS) located at the Paul Scherrer Institute (PSI). This analytical method is highly adequate for investigation of combustion processes in low-pressure flames [29–32]. In particular, the capability to identify reactive intermediates, such as radicals, isomer-selectively by photoion mass-selected threshold photoelectron spectra (ms-TPES) has proven to be useful when sampling from reactive environments (e.g., pyrolysis, photolysis, or catalytic reactors [33,34]), even though scanning the photon energy is time consuming and the mass resolution of the instrument is limited compared to other mass spectrometric systems [35].

In this work, the iPEPICO setup is used to investigate the abstraction of chemically different hydrogen atoms from the hydrocarbon fuels in low-pressure hydrogen flames doped with the different alkanes and alkenes. Ethane, *n*-butane and *i*-butane were specifically targeted in a systematic approach to investigate the hydrogen atom abstraction of primary, secondary, and tertiary hydrogen atoms. In addition, 1-butene, *i*-butene, and tetramethylethylene were chosen to evaluate the abstraction of allylic and vinylic hydrogen atoms. This set of fuels allows for comparison of different reaction pathways and enables a systematic experimental approach by measuring, identifying, and quantifying the fuel radicals in low-pressure flames. Hydrogen was chosen as base fuel to provide sufficient H atoms as well as OH radicals and to increase the role of hydrogen abstraction or addition in the fuel destruction pathways.

2. Experimental

Detailed information about the iPEPICO setup used in this study is available in the literature [36] and the coupling to the flame experiment has been described in [29]. In brief, a premixed

McKenna-type flat-flame burner with a 6 cm diameter bronze matrix was installed in a low-pressure (40 mbar) flame chamber. The gas sample was withdrawn from the flame at the centerline of the burner by a quartz nozzle. The distance between burner and nozzle tip was varied with a stepper motor to record spatial species profiles.

A molecular beam is formed at the nozzle and passes through a nickel skimmer. Due to the rapid expansion in the molecular beam, reactions are quenched immediately, and the detection of reactive species is possible. A schematic of this low-pressure flame setup is shown in the supplemental material. The pressures are 10^{-4} mbar in the first pumping stage and 10^{-6} mbar in the ionization chamber. Ionization of the flame-sampled molecules was performed by tunable VUV synchrotron radiation in the range of 60–250 nm (5–21 eV) at a resolving power of $E/\Delta E = 1500$, as provided by a 150 lines mm^{-1} grating. Higher harmonic radiation was absorbed by a gas filter (Ne or Ar/Kr) or a MgF_2 window depending on the actual photon energy.

Ions and electrons are detected in delayed coincidence using velocity map imaging and time-of-flight mass spectrometry. A multistart-multistop [37] approach was applied to correlate electrons and ions. Species are identified at a constant burner position, while the photon energy was scanned over the ionization threshold of interest and photoelectrons and photoions are recorded in coincidence. Electrons without kinetic energy hit the center of the detector. Electrons with kinetic energies are imaged as concentric rings with increasing diameter for ionization events with increasing difference between photon energy and ionization threshold. Electrons with more than 1 eV kinetic energy are not detectable. This causes a non-linear electron loss effect, which must be corrected or only measurements below 1 eV above the ionization threshold can be used for quantitative evaluation based on literature ionization cross sections. Mass-selected photoionization efficiency (PIE) spectra (not shown in this work) or threshold photoelectron spectra (ms-TPES) (near zero kinetic energy; $E_{\text{kin}} > 30$ meV) with a resolution of better than 5 meV, which is superior to conventional ultraviolet photoelectron spectra (UPS), were obtained by selecting the electron signal measured in coincidence with the ions in the m/z range of interest.

The mass separation of the photoions was performed by time-of-flight (TOF) analysis with a mass resolution of $m/\Delta m = 300$. Quantitative evaluation of species concentrations or mole fractions is based on the ion signal (for a specific m/z) recorded at specific photon energies in coincidence with all detectable electrons. Spatial species profiles are measured as a function of the distance between the sampling nozzle and the burner surface, also known as height above burner (HAB), with constant photon energy. Photon energies were chosen so that no electron losses had to be considered for the profiles shown in this work.

Hydrogen flames were doped with the respective hydrocarbon fuels and had the same stoichiometry of $\Phi = 1.25$. Conditions were chosen to keep the carbon flow, the stoichiometry, and the C/H/O ratio constant. Because of the almost identical reaction enthalpy of the reactant mixture, the flame temperature is expected to be similar for all flames. Calibrated mass flow controllers metered the gas flows with an absolute uncertainty of $\pm 5\%$. The pressure in the burner chamber was set to 40 mbar for all flames and controlled by a throttle valve with an accuracy of ± 0.1 mbar. The investigated flame conditions are summarized in Table 1.

3. Data analysis

Quantitative data analysis follows previous works of Oßwald et al. [29] and Cool et al. [38]. Ion signals of interest are integrated over a single (nominal) m/z ratio. For ms-TPES, the ions are restricted to coincidences with threshold electrons. Because energetic

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