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Proceedings of the Combustion Institute 31 (2007) 565–573
Proceedings of the Combustion Institute
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Benzene precursors and formation routes in a stoichiometric cyclohexane flame ☆

Matthew E. Law [a], Phillip R. Westmoreland [a,*], Terrill A. Cool [b], Juan Wang [b], Nils Hansen [c], Craig A. Taatjes [c], Tina Kasper [d]

[a] *Department of Chemical Engineering, University of Massachusetts, Amherst, MA 01003, USA*
[b] *School of Applied and Engineering Physics, Cornell University, Ithaca, NY 14886, USA*
[c] *Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551, USA*
[d] *Physikalische Chemie 1, Universität Bielefeld, D-33501 Bielefeld, Germany*

Abstract

Benzene formation was found to be dominated by stepwise radical dehydrogenation of cyclohexane in a stoichiometric flat flame of cyclohexane/O_2/32.5% Ar, 30.00 Torr pressure, and 35.0 cm s^{-1} feed velocity. This route, involving H-abstractions and β-scissions, is in contrast to conventional propargyl routes. Three types of analyses lead to this conclusion: identification of key flame species by mass and ionization energy; measurement and use of mole-fraction profiles in the flat flame; and mechanistic reactive-flow modeling of the flame, interpreted by analyzing the dominant reaction steps giving rise to the prediction. For relevant species, profiles of mole fraction were mapped by molecular-beam mass spectrometry in separate apparatuses with identical burners using electron ionization (UMass Amherst) and synchrotron VUV photoionization (LBNL ALS), respectively. In the latter, recently developed apparatus, ionization energies can be measured with greatly enhanced resolution, yielding improvements in species identification that include precise resolution of hydrocarbon isomers, crucial to the findings of this study.

Keywords: Cyclohexane; Molecular-beam mass spectrometry; Flames; Benzene; Dehydrogenation

1. Introduction

Because combustion of fuels can lead to the formation of benzene, polycyclic aromatic hydrocarbons (PAH), and soot, understanding their formation and destruction is important for understanding the effects of combustion on health, safety, and the environment. Some PAH such as benzo(a)pyrene are known carcinogens [1] and some can be mutagenic [2]. PAH are also chemical intermediates in the formation of soot, which can be suspended in the air, inhaled, and then lodged in the lungs. To control these pollutants, it is important to understand how the first ring is formed because this step is thought to be rate-limiting for subsequent PAH and soot formation [3].

Cyclohexane combustion produces an increased amount of benzene [4] in comparison to other aliphatic fuels, but it has been uncertain why. The focus of the last 30 years has been on growth routes to the first ring from smaller species, where propargyl (C_3H_3) self-combination is

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☆ Supplementary data for this article can be accessed online. See Appendix A.

[*] Corresponding author. Fax: +1 413 545 1647.
E-mail address: westm@ecs.umass.edu (P.R. Westmoreland).

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doi:10.1016/j.proci.2006.07.259

now commonly accepted as a prominent route from many fuels at different combustion conditions [5–9].

Based on cyclohexane destruction pathways, formation of benzene in a stoichiometric cyclohexane flat flame had been expected to be similar to that in ethylene and 1,3-butadiene flames, where it is dominated by $C_3H_3 + C_3H_3$. Law et al. [10] found the main destruction route of cyclohexane was formation and beta-scission of the cyclohexyl radical, eventually forming 1,3-butadiene, vinyl, and ethylene:

$$\text{cyclohexane} + R \leftrightharpoons \text{cyclohexyl} + RH \quad (R1)$$

$$\text{cyclohexyl} \leftrightharpoons \text{5-hexenyl} \quad (R2)$$

$$\text{5-hexenyl} \leftrightharpoons \text{3-butenyl} + C_2H_4 \quad (R3)$$

$$\text{3-butenyl} \leftrightharpoons \text{1,3-butadiene} + H \quad (R4)$$

$$\text{1,3-butadiene} + H \leftrightharpoons C_2H_3 + C_2H_4 \quad (R5)$$

$$C_2H_3 \leftrightharpoons C_2H_2 + H \quad (R6)$$

McEnally and Pfefferle [11] showed that benzene was mainly formed via addition reactions rather than by dehydrogenation in non-premixed cyclohexane flames. However, there was previous evidence from several near-stoichiometric combustion experiments that cyclohexane dehydrogenation may be important, including a rapid compression machine, $\phi = 1.0$ [12]; a jet-stirred reactor, $\phi = 0.5$–1.5 [13]; and a single-cylinder internal combustion engine, $\phi = 1.0$ [14].

The present work establishes that benzene can be formed in a flame by successive radical dehydrogenation steps from cyclohexane, completely dominating small-molecule growth routes in this flame. This finding is supported by identification and measurement of isomeric flame species with a recently developed molecular-beam mass spectrometry (MBMS) method using synchrotron VUV photoionization, combined with flat-flame modeling. The data are unique in being able to establish the finding by crucial isomer identification and mole-fraction profiles.

2. Experimental methods and model

Laminar, premixed, stoichiometric cyclohexane flames were stabilized on a flat-flame (McKenna) burner of 6.03 cm diameter. Stoichiometric conditions were chosen so that benzene would be destroyed primarily by oxidation rather than by growth to higher-molecular-weight species. Cyclohexane was metered with a syringe pump, vaporized, and mixed to generate the feed of 6.75 mole% cyclohexane (c-C_6H_{12}), 60.75% O_2, and 32.5% Ar. Operating conditions were chosen to optimize flame stability, standoff, and thickness: 30.00(±0.01) Torr and 35.0 cm s^{-1} (at 300 K) feed-gas velocity, corresponding to mass flux of 0.00214 g cm^{-2} s^{-1}.

Two different, complementary MBMS systems were used. Many mole-fraction profiles were measured using a photoionization MBMS system at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory [15]. Profiles of H, CH_2, CH_3, CH_4, O, and OH mole fractions, temperature, and area-expansion ratio were measured in an MBMS system located at the University of Massachusetts Amherst (UMass) [5].

Temperature was measured using a 0.076-mm-diameter, butt-welded, beadless Pt/Pt–13% Rh thermocouple coated with a 4.5 wt% BeO–95.5% Y_2O_3 ceramic coating. For radiation compensation, resistance heating was generally used to 1900 K, calibrated in high vacuum; for higher temperatures, emissivity was determined from the lower-temperature measurements. The maximum temperature is 1950 K at 7.0 mm, decreasing to 1650 K at 26 mm.

Area-expansion ratio was measured by hot-wire anemometry of cold gases at the same Reynolds numbers as the flame gases. Additional details are presented elsewhere [10,15,16].

Hybrid-angle quartz sampling probes [17] with 40° tips were used to sample species from the flame. These probes provide minimal perturbation of the flame. However, no measurements are presented closer than 0.7 mm because the flame is perturbed at such close positions; however, positive gradients must necessarily occur near the surface for non-feed species. Orifice diameters were 0.22 mm (UMass) and 0.35 mm (ALS). Beyond the sampling nozzle, sampled gas expands and cools in a 10^{-5} Torr region, reaches free molecular flow, and is collimated into a molecular beam by a 2-mm skimmer.

In the ALS apparatus (Fig. 1), the molecular beam is photoionized by synchrotron-generated VUV photons for time-of-flight mass spectrometry. Photon energies are selected precisely by a 3-m monochromator with maximum resolving power of $E/\Delta E = 400$. Ionized species are pulsed at 15 kHz into a flight tube, where ions are separated by their mass-to-charge ratios (m/z). A microchannel-plate detector with fast time response amplifies the signal, which is collected and binned by a multi-channel scaler. In the UMass apparatus, electron ionization and quadrupole mass spectrometry were used.

Photoionization efficiency (PIE) curves of ionization signal vs. photon energy were measured initially to determine appropriate photon energies for profile measurements. These photon energies were chosen to be above the ionization threshold for singly charged molecular ions (thus, subsequent discussion will refer to mass rather than