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Proceedings of the Combustion Institute 32 (2009) 453–460

Proceedings of the Combustion Institute

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Shock tube and modeling study of isobutene pyrolysis and oxidation

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Abstract

Pyrolysis and oxidation of isobutene were studied behind reflected shock waves in the temperature range 1000–1800 K at total pressures between 1.0 and 2.7 atm. The study was carried out using following method: (1) a single-pulse technique for product yields, (2) time-resolved IR-laser absorption at 3.39 μm for isobutene decay and formation rates of compounds which contain C–H bond, (3) time-resolved IR emission at 4.24 μm for CO_2 formation rate, and (4) time-resolved UV absorption at 306.7 nm for OH radical formation rate. The pyrolysis and oxidation of isobutene were modeled using a reaction mechanism including the sub-mechanisms for methane, acetylene, ethylene, ethane, formaldehyde, allene, propyne, propene, and ketene oxidation. The reaction mechanism used in the present study could reproduce all experimental results.

Keywords: Shock tube; Isobutene; Reaction mechanism; High temperature

1. Introduction

Isobutene is an important intermediate [1] of the pyrolysis and oxidation of branched alkanes such as iso-octane. The pyrolysis and oxidation of ETBE, which is used as octane enhancer worldwide, also produces significant amount of isobutene. Therefore, kinetic modeling in the combustion of the fuels requires a reliable mechanism and rate constant expressions for the pyrolysis and oxidation of isobutene.

Several researchers studied isobutene pyrolysis and oxidation. Bradley et al. [2] modeled shock tube pyrolysis of isobutene, and Brezinsky and Dryer [1] studied oxidation in a turbulent flow reactor. Tsang et al. [3] measured the rate constants on the reactions for isobutene + H in a shock tube. Curran et al. [4] measured and modeled ignition delays of isobutene behind reflected shock waves. Dagaut et al. [5] studied the oxidation of isobutene over a wide range of conditions with jet stirred reactor. Bauge et al. [6] measured

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doi:10.1016/j.proci.2008.06.144

and modeled ignition delays behind reflected shock waves and product distributions obtained with perfect stirred reactor. Santhanam et al. [7] observed the initial decomposition of isobutene behind incident shock waves with laser shlieren technique.

The purpose of this work is to investigate the mechanism and the rate constants for the pyrolysis and oxidation of isobutene comparing to the previous reports [2–4,6,7] at high temperatures above 1000 K.

2. Experimental

Three shock tubes with 4.1 cm i.d. were used in this study. Since these shock tubes [8–11] were described in detail previously, the simple description is given below. The first was a magic-hole-type shock tube, which had the facility for single-pulse technique. The reacted gas mixtures were analyzed by gas-chromatographs (GCs) with a thermal-conductivity detector. An effective heating time t_e (reaction time), which was defined as the time between the arrival point of the reflected shock front and the 80% point in the fall from the reflected shock front pressure, was determined with an accuracy of ±5% using the method described previously [8,9]. Assuming that the reaction was frozen perfectly at the effective heating time, the concentration of carbon-containing compounds was compared with those simulated.

The second was a standard-type shock tube connected to laser absorption and IR emission equipment [12,13]. The transmitted light intensity of a 3.39-μm He–Ne laser beam through a 4.1-cm path-length in the shock tube and through an interference filter ($\lambda_{max} = 3.39$ μm, half-width = 0.072 μm) was monitored with an InSb detector, using the same method used previously [12,13]. The 3.39 μm laser beam was absorbed by many compounds containing C–H bond, but mainly by isobutene, C_2H_6, and CH_4 under our experimental conditions in this study. The equations between the extinction coefficient of each species and temperature measured were used for simulations. In this experiment, an IR emission at 4.24 μm was monitored with the InSb detector through a CaF_2 window, an interference filter $\lambda_{max} = 4.24$ μm, half-width = 0.1 μm and two slits with widths 0.8 mm at each end of a cylindrical tube of length 2 cm in order to trace the formation of CO_2. The relative emission at 4.24 μm comes from not only CO_2, but also CH_2CO and CO under our experimental conditions. The relative emission intensity of these compounds against temperature was measured and shown in Ref. [11].

The third was a standard-type shock tube connected with UV absorption equipment similar to that previously reported [9,11,13]. To observe the absorption profile due to OH radical, a light at 306.7 nm was obtained by microwave discharge of H_2O in He. The transmitted light intensity at 306.7 nm through a 4.1 cm path-length in the shock tube, dispersed by a grating monochromator, was monitored with a photomultiplier, using the same method used previously [13].

Gas mixtures were prepared manometrically. The compositions of reaction mixtures are shown in the supplemental file. The error in the isobutene, hydrogen, and oxygen fraction was less than ±2% of the respective fraction. The initial pressure (P_1) of the gas mixtures was 50 ± 0.1 Torr. The Ar (Teisan Co.), H_2 (Chuunenfaiingasu Co.), and O_2 (Seitetsu Kagaku Co.) specified to be 99.999%, 99.99%, and 99.995% pure, respectively, were used without further purification. The isobutene (Tokyo Kasei Kogyo Co.), specified to be 99% pure, was frozen, degassed a number of times and purified by trap-to-trap distillation before use.

All temperatures and pressures were calculated from the incident shock velocity with the initial pressure (P_1) and temperature (T_1) assuming full vibrational relaxation without chemical reaction. The uncertainty in the calculated temperatures is considered to be ±1.2%. The computer simulation in this study was essentially the same as described previously [9–16]. The computer routine was a Gear-type integration of a set of differential equations describing the chemical kinetics under constant density conditions for a reflected shock wave [15,16]. Reverse reactions were automatically included in the computer program through equilibrium constants calculated from thermochemical data [15,16]. Temperatures in the reaction zone were considered to change with reaction progress under our experimental conditions.

Sensitive spectra (pS) were calculated in order to determine the importance of each reaction. The pS was defined as $pS_{ij} = \log[(\text{computed quantity})j'/(\text{computed quantity})j]/\log[(\text{parameter})i'/(\text{parameter})i]$, where the primes denote the parameters i and computed quantities j for a computer simulation in which the value of one parameter has been changed from a reference value (unprimed quantity and parameter) [17].

3. Results

3.1. Pyrolysis

The product distributions by GCs for A (1.0% *iso*-C_4H_8 in Ar) are shown in Fig. 1a. The main products detected were CH_4, C_2H_6, C_2H_4, C_2H_2, p-C_3H_4(propyne), a-C_3H_4 (allene), C_3H_6, 1,3-C_4H_6, and C_6H_6. The species, C_4H_4(vinylacetylene), 1,2-C_4H_6, and C_4H_2 were also detected in smaller quantities: each was below 5% of the initial concentration of isobutene.