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# Experimental and kinetic modeling study of butene isomer pyrolysis: Part II. Isobutene

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ABSTRACT

The pyrolysis of isobutene was investigated using a tubular flow reactor at an absolute pressure of ~0.82 atm over a temperature range of 610–860 °C with residence times ranging from ~0.5 to ~2.4 s. The initial concentration of the fuel ranged from 5 to 50 mol%. These data were compared to the predictions of a fundamentally based detailed kinetic model. The model accurately predicted the observed fuel conversion, production of light products, and the formation of several important molecular weight growth species. The primary pathways that lead to the fuel decay and the formation of major products are discussed. In particular, H-atom abstraction from isobutene results in the formation of the 2-methyl allyl radical, which undergoes a $\beta$-scission reaction to form allene plus methyl. The subsequent addition reaction of 2-methyl allyl to allene is energetically favored and provides a route to the formation of stable molecular weight growth products that are readily converted to benzene and toluene. The potential energy surface for this reaction was derived from CBS-QB3 calculations and the corresponding temperature and pressure dependent rate constants are obtained. The model predictions were also compared and generally are in good agreement with multiple published isobutene pyrolysis data sets that were measured under significantly different conditions.



## 1. Introduction

Recent investigations on the combustion of the butanol isomers, tertbutanol and isobutanol [1–10], have demonstrated the importance of the reaction subset of isobutene. Isobutene is also an important intermediate in the pyrolysis and oxidation of branched alkanes such as isobutane [11–13] and isooctane [14,15]. The pyrolysis and oxidation of octane enhancers and antiknock additives such as methyl tert-butyl ether (MTBE) [16–19] and ethyl tert-butyl ether (ETBE) [20–22] also produce significant amounts of isobutene. For these reasons, there are more studies addressing the pyrolysis [23–31], oxidation [15,32–35], and combustion [36–38] of isobutene, compared to the two linear butene isomers.

Most of the prior studies have focused on low levels of fuel conversion, and only a few were able to characterize the molecular weight growth (MWG) chemistry. Dagaut et al. [33] used gas chromatographic analysis to measure the concentration profiles for several $C_4$–$C_6$ MWG products during the oxidation of isobutene in a jet-stirred reactor at temperature range of ~800–1230 K with pressure of 1, 5, and 10 atm. The proposed reaction mechanism delineated two routes for the formation of benzene: the addition of propargyl radicals to allene and the recombination of propargyl radicals. However, the model under predicted the formation of several $C_5$ products. Yasunaga et al. [30] studied the pyrolysis and oxidation of isobutene behind reflected shock waves in the temperature range 1000–1800 K at total pressures between 1.0 and 2.7 atm. The production profiles of 1,3-butadiene and benzene were measured as a function of temperature. Zhang et al. [31] provided isomer-selective speciation of several products that were formed during the pyrolysis of isobutene at low pressure (~3–11 torr) in the temperature regime between 900 and 1900 K. In addition to several light products, they observed the formation of 1,3-butadiene, 1,3-cyclopentadiene, and benzene. Schenk et al. [37] conducted detailed mass spectrometric and modeling study of laminar premixed low-pressure (40 mbar) flat argon-diluted (25%) flames of isobutene under fuel-rich conditions. Multiple $C_5$ species were identified and measured, but the model only provided qualitative descriptions of these products. Al Shoaibi et al. [13,39] detected multiple MWG species up to $C_{10}$ during the flow reactor pyrolysis of the butene isomers at temperatures of 825–1025 K under atmospheric pressure. The modeling results indicated that more work was needed especially regarding the characterization of MWG kinetics.

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Similar to the pyrolysis of other olefins, resonantly-stabilized radicals are expected to be present in relatively high concentrations during isobutene pyrolysis. In particular, 2-methyl allyl is formed from the dissociation and H-abstraction from the parent and should be important. Some researchers [30,31,37] have suggested that 2-methyl allyl ($C_2$•C=C) isomerizes to its linear isomer, methyl allyl (CC=CC•), which then dissociates to 1,3-butadiene plus H. However, the unimolecular dissociation of 2-methyl allyl to form methyl and allene is favored relative to the isomerization. Allene may readily isomerize to propyne. The 2-methyl allyl radical can add to the reactant or product olefins and dienes, or to triple bonds in alkynes. Yasunaga et al. [30] included the addition of 2-methyl allyl to propyne in their mechanism to explain the formation of benzene, although the process was represented as one global reaction ($C_2$•C=C + C≡CC → $C_6H_6 + H_2 + CH_3$). A study by Merchant et al. [1] on the pyrolysis of isobutanol from 900 to 1100 K at 1.72 atm, under conditions where significant amounts of isobutene were produced, found that the formation of soot precursors (e.g., benzene, toluene, and 1,3-cyclopentadiene) depends strongly on pressure dependent reactions involving 2-methyl allyl radical.

In this work we investigate the pyrolysis kinetics of isobutene under conditions that lead to significant MWG product formation. (This effort complements our first paper in this series that discussed the results for 1- and 2-butene pyrolysis [40].) Flow reactor experiments were performed at an absolute pressure of ~0.83 atm. The temperature (610–860 °C), extent of inert gas dilution (~95%, 90%, and 50%), and nominal hot zone residence time (~0.5, ~1.2, and ~2.4 s) were varied. The fuel conversion ranged from virtually no reaction to ~90%. The light products and several MWG products were quantified. The measured mole fractions exhibit consistently good carbon and hydrogen mass balances. These data are compared to the predictions of a fundamentally based detailed kinetic model that was developed to describe the pyrolysis of the three butene isomers. The unadjusted model was able to capture the fuel conversion, formation of light species, and production of several MWG products. The model was then applied to three sets of isobutene pyrolysis data in the literature [28,30,31] that were collected under significantly different conditions, with generally good agreement.

## 2. Methods

### 2.1. Experimental specifications

Isobutene pyrolysis experiments were conducted using a continuous flow tubular reactor. Details of the experimental apparatus and procedures have previously been described [41] and therefore only a brief description is given here. A known flow rate of the isobutene (Matheson TriGas, 99.5%) in nitrogen (General Air, 99.998%) was introduced into a 6 mm ID tubular quartz reactor that was heated in an electric furnace. The temperature profile of the reactor was measured axially along the length of the reactor using a K-type thermocouple; these profiles are provided in a parallel study for the pyrolysis of 1- and 2-butene [40]. The reproducibility of the measurements are ±2 °C in the center, constant temperature region of the reactor. At the edges of the reactor, where the temperature is lower, the error in the measurement is higher. Experiments were conducted at an ambient (high-altitude) pressure of ~0.82 atm. The initial isobutene concentration was set at 5%, 10%, or 50% mole in $N_2$. The total flow rate was 30, 60, or 150 SCCM, which corresponds to nominal residence times of approximately 2.4, 1.0, and 0.5 s, respectively, in the center constant temperature region of the reactor. The summary of the experiment conditions for each dataset is provided in Table S1 in the SI.

The fuel and $N_2$ were well mixed before they were introduced into the reactor. The reaction gas stream was analyzed using gas-chromatography (GC). Nitrogen, hydrogen, and light hydrocarbons were detected using a thermal conductivity detector (TCD). All hydrocarbons were quantified using a flame ionization detector (FID) that was connected in parallel with a mass spectrometer that allowed for product identification. The response factors were calibrated using both commercial and in-house-prepared standard mixtures. The FID response factors of species that were not calibrated directly were estimated based on a correlation of response factors to the number of carbon atoms in the species. One limitation to the analytical method is that some isomer pairs (1-butene and isobutene, 1,3-methylcyclopentadiene and 2,4-methylcyclopentadiene, and 1,3-cyclohexadiene and 1,4-cyclohexadiene) are not completely separated from one another and in these cases, the sum of the two species is reported. Since the response factors for these sets of species are similar, the impact on the total mass balance is negligible. For the case of 1-butene and isobutene, the relative amount of 1-butene is small compared to the amount of isobutene. This will be discussed in more detail below.

### 2.2. Kinetic modeling

The detailed kinetic mechanism that was used in this study was also used to describe the pyrolysis of 1- and 2-butene [40] and the mechanism and thermodynamic files are provided therein. The details of the mechanism development process are provided therein [40] and in an earlier analysis of propylene pyrolysis [41]. Simulations were performed using the plug flow reactor module in Chemkin Pro [42]. This program was used to generate concentration-time/temperature profiles, rates of production plots, and sensitivity analysis. In many instances, the mechanism was specified in an irreversible format (i.e., the forward and reverse reactions are both explicitly specified) to allow for partially equilibrated reactions to be identified in both rate and sensitivity analyses. Note that in either format, reversible or irreversible, the reverse rate constants were calculated from the thermodynamic database and both formats predict identical concentration-time/temperature profiles.

In several places throughout the text, tables, and figures, we employ a simplified chemical notation that omits the hydrogen atoms. For $C_3$ and larger species, the radical site is indicated by "•", a double bond by "=", a triple bond by "≡", and a cyclic species by "cy".

## 3. Results

The results for each set of experiments are provided in the SI (Tables S2–S8). Each data point is an average of at least three measurements. The standard deviations of the measurements for concentrations above 0.1 mol% was typically ~0.5% of the average value; for lower concentration species, the deviation usually ranged from ~2% to 6% of the average. The change in the measured mole fractions is due to both reaction and dilution since the total number of moles changes during the reaction. The impact of dilution can be assessed from the change in the $N_2$ mole fraction since the number of moles of $N_2$ remains constant. The majority of the products were identified. For the few species that remain unidentified, the molecular formula is known. For the experiments where the initial fuel concentration was either 50 or 10 mol%, the sum of the mole fractions and carbon and hydrogen balances are within the experimental uncertainty (±0.02). This suggests that essentially all of the products that are produced in the reactor, even the heavy ones, made it to the GC sample loop and that they were accurately