

A high-temperature shock tube kinetic study for the branching ratios of isobutene + OH reaction

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Abstract

Isobutene is an important intermediate formed during the oxidation of branched alkanes. It also appears as a byproduct during the combustion of methyl-tert-butyl-ether (MTBE) which is used as octane enhancer in gasolines. To understand better the oxidation kinetics of isobutene, we have measured the rate coefficients for the reaction of OH radicals with isobutene ($\text{H}_2\text{C}=\text{C}(\text{CH}_3)_2$) behind reflected shock waves over the temperature range of 830–1289 K and pressures near 1.5 atm. The reaction progress was followed by measuring mole fraction of OH radicals near 306.7 nm using UV laser absorption technique. Three deuterated isotopes, isobutene-1-d2 ($\text{D}_2\text{C}=\text{C}(\text{CH}_3)_2$), isobutene-3-d6 ($\text{H}_2\text{C}=\text{C}(\text{CD}_3)_2$) and isobutene-d8 ($\text{D}_2\text{C}=\text{C}(\text{CD}_3)_2$) were employed to elucidate branching ratios of the allylic and vinylic H-abstraction from isobutene by OH radicals. H-abstraction from the allylic sites was found to be dominant and constituted about 75% of the total rate in the entire temperature range of the current work. The derived three-parameter Arrhenius expressions for site-specific H- and D- abstraction rates over 830–1289 K are (units: $\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$):

$$k_{3,\text{H}} = 6.98 \times 10^6 \left(\frac{T}{\text{K}}\right)^{1.77} \exp\left(-\frac{136.6 \text{ K}}{T}\right)$$

$$k_{3,\text{D}} = 4.42 \times 10^6 \left(\frac{T}{\text{K}}\right)^{1.8} \exp\left(-\frac{361.7 \text{ K}}{T}\right)$$

$$k_{1,\text{H}} = 6.25 \times 10^5 \left(\frac{T}{\text{K}}\right)^{2.16} \exp\left(-\frac{711.6 \text{ K}}{T}\right)$$

$$k_{1,\text{D}} = 3.13 \times 10^7 \left(\frac{T}{\text{K}}\right)^{1.67} \exp\left(-\frac{1814 \text{ K}}{T}\right)$$

The subscript of k identifies the position of H or D atom in isobutene according to the IUPAC nomenclature of alkenes.

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1. Introduction

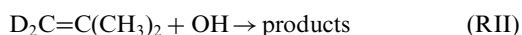
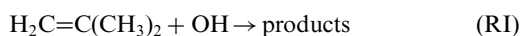
Isobutene ($\text{H}_2\text{C}=\text{C}(\text{CH}_3)_2$) is the smallest branched alkene which appears as an important intermediate species during the combustion of long-chain branched alkanes [1]. Isobutene is produced in large concentration during the pyrolysis and oxidation of methyl-tert-butyl-ether (MTBE) and ethyl-tert-butyl-ether (ETBE) [2]. Both of these ethers are widely used for gasoline reformulation to boost the octane number [3]. Isobutene is also a precursor to the formation of polycyclic aromatic hydrocarbons and soot particles [4]. The chemistry of isobutene is an essential component of the chemical kinetic mechanisms of large hydrocarbons and oxygenated fuels. Therefore, it is crucial to understand the oxidation pathways of isobutene for the hierarchical development of detailed chemical kinetic models.

Compared to normal alkanes and normal alkenes, limited experimental and modeling kinetic studies are available in the literature for branched alkenes. The pyrolysis of isobutene has been studied by few research groups [5–8]. Santhanam et al. [6] used laser-schlieren technique to identify the role of various channels involved during the pyrolysis of isobutene at high temperatures ($T \geq 1600$ K). They concluded that the sole dissociation channel is the simple C–H bond fission of isobutene to produce isobutenyl (C_4H_7 , 2-methyl-allyl) radical that further dissociates rapidly into CH_3 and allene (C_3H_4). The oxidation kinetics of isobutene has also been the focus of several studies [3,9–15]. Dagaut and Cathonnet [3] studied the oxidation of isobutene using jet-stirred reactor at temperatures ranging 800–1230 K and pressures of 1, 5 and 10 atm. They were able to predict their measured species profiles using a detailed kinetic model that consisted of 110 species and 743 reactions. More recently, Yasunaga et al. [12] studied the products of pyrolysis and oxidation of isobutene behind reflected shock waves over 1000–1800 K using gas chromatography, IR laser absorption/emission and UV absorption. They found isobutene to be relatively thermally stable ($\tau = 0.15$ s at 1300 K). They proposed a reaction mechanism comprising of 304 reaction steps and 72 species which reproduced their experimental results reasonably well. They identified H-abstraction reaction of isobutene by OH radicals to be one of the most sensitive reactions during the oxidation of isobutene. The group of Henry Curran at NUIG has recently conducted a wide-ranging theoretical and chemical kinetic modeling study of isobutene oxidation [10] that included ignition delay time, flame speed and species ($i\text{-C}_4\text{H}_8$, C_3H_6 , C_3H_4 , CH_4 , CO etc.) measurements. Their optimized mechanism for the oxidation of isobutene is comprised of more than 2400 reactions and 460 species.

The reaction of isobutene with OH radicals has been investigated theoretically and experimen-

tally by several groups [13–21]. Most of these studies were focused at temperatures less than 400 K. Smith [13] measured the rate coefficients of the reaction of OH with isomers of butene, including isobutene, at 1259 K using flash photolysis/laser fluorescence technique. Smith found that the measured rate coefficients for OH + butenes are faster than OH + ethene. He concluded that the rate coefficient increases with the increase in the number of allylic H atoms and that the contribution of vinylic H atoms to the total rate is small. There are only two theoretical reports [17,18] on the reaction of isobutene with OH radicals under combustion relevant temperatures. Huynh et al. [17] estimated the rate coefficients for vinylic H-abstractions of OH + alkene reaction systems by employing reaction class transition state theory (RC-TST) combined with the linear energy relationship and the barrier height grouping methods. Sun and Law [18] computed the rate coefficients for reactions of OH radicals with butene isomers using CCSD(T)/6-311++G(d,p)//BH&HLYP/6-311G(d,p) quantum chemical and transition state theory methods. The results revealed that allylic H-abstraction channels are dominant and can occur either directly or *via* complex forming mechanism [18]. For the OH + isobutene reaction, they calculated the rate coefficient of allylic H-abstraction and found a value of 8.3×10^{12} $\text{cm}^3\text{mol}^{-1}\text{s}^{-1}$ at 1259 K. Their calculated value is two times lower than the experimental value reported by Smith [13]. Additional experimental and/or theoretical work was suggested to further understand isobutene + OH system.

Isobutene offers two types of H atoms, namely allylic and vinylic, to be abstracted by important combustion radicals such as OH, H, O, CH_3 and HO_2 . Hydrogen abstraction from the vinylic site results into the formation of 2-methyl-1-propenyl ($\bullet\text{HC}=\text{C}(\text{CH}_3)_2$) radical, whereas H-abstraction from the allylic site forms resonantly stabilized 2-methyl-allyl ($\text{H}_2\text{C}=\text{C}(\bullet\text{CH}_2)\text{-CH}_3$) radical. Allyl radicals play pivotal role in combustion chemistry as they are radical scavengers. We had previously used deuterated kinetic isotope effect to experimentally determine branching ratios of allylic and vinylic H-abstractions for the propene + OH system [22]. Some differences were, however, observed with theoretical predictions [24], particularly on the contribution of vinylic H-abstraction. Aiming to investigate this further, in the current work, we have investigated the reaction of OH with the deuterated isotopes of isobutene to extract the branching ratios of vinylic and allylic H-abstraction by OH. The following reactions are investigated using shock tube and laser absorption technique:



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