# H Atom Attack on Propene

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Supporting Information

**ABSTRACT:** The reaction of propene (CH<sub>3</sub>CH=CH<sub>2</sub>) with hydrogen atoms has been investigated in a heated single-pulsed shock tube at temperatures between 902 and 1200 K and pressures of 1.5–3.4 bar. Stable products from H atom addition and H abstraction have been identified and quantified by gas chromatography/flame ionization/mass spectrometry. The reaction for the H addition channel involving methyl displacement from propene has been determined relative to methyl displacement from 1,3,5-trimethylbenzene (135TMB), leading to a reaction rate,  $k(H + \text{propene}) \rightarrow H_2C=CH_2 +$  $CH_3) = 4.8 \times 10^{13} \exp(-2081/T) \text{ cm}^3/(\text{mol s})$ . The rate constant for the abstraction of the allylic hydrogen atom is determined to be  $k(H + \text{propene} \rightarrow$  $CH_2CH=CH_2 + H_2) = 6.4 \times 10^{13} \exp(-4168/T) \text{ cm}^3/(\text{mol s})$ . The reaction of H + propene has also been directly studied relative to the reaction of H + propyne, and the relationship is found to be  $\log[k(H + \text{propyne} \rightarrow \text{acetylene} +$  $CH_3)/k(H + \text{propene} \rightarrow \text{ethylene} + CH_3)] = (-0.461 \pm 0.041)(1000/T) +$ 



 $(0.44 \pm 0.04)$ . The results showed that the rate constant for the methyl displacement reaction with propene is a factor of  $1.05 \pm 0.1$  larger than that for propyne near 1000 K. The present results are compared with relevant earlier data on related compounds.

## INTRODUCTION

Liquid fuels are comprised of unsaturated and saturated normal, branched, and cyclic—hydrocarbons. An alkyl radical is formed when a fuel molecule decomposes upon radical attack or thermal excitation. The alkyl radical can breakdown via  $\beta$ -bond scission to produce another alkyl radical and a 1-alkene molecule. Propene is the simplest substituted of the 1-alkenes. As the fuel breakdown progresses via unimolecular reactions and oxidation steps, H atoms are produced. They are among the most important intermediates in hydrocarbon combustion.

This paper is concerned with the reaction of H atoms with propene, studied under shock-tube conditions. It is an extension of earlier measurements of the mechanism and rate constants for the reaction of H atoms with other unsaturated hydrocarbons. These reactions are of particular importance with respect to the mechanisms associated with the formation of the initial aromatic ring and subsequent soot formation. H-atom reaction with larger unsaturated hydrocarbons leads to resonance stabilized radicals, such as allyl, benzyl, and propargyl radicals. They are intermediates in the cyclization steps that initiate the production of aromatic rings, as precursors of polycyclic aromatic hydrocarbons (PAHs) and soot. Under fuel-rich conditions, the concentrations of these radicals can build up in combustion systems.

The reactivity of H-atoms is such that their attack on any hydrocarbon of even moderate complexity leads to multiple reaction channels. In the case of unsaturated hydrocarbons (always present in high temperature rich systems) there are contributions from abstraction as well as addition channels. Their relative importance dictates the reaction pathways for subsequent chemical processes. For H-atom attack on propene the reaction channels in Scheme 1 should be considered.

Reaction 1 involves terminal H-addition to propene to produce an isopropyl radical. Previous work of the unimolecular decomposition of *iso*- $C_3H_7$  has shown that at high temperatures relevant to combustion, reaction 1 is reversible, favoring back decomposition into propene and H (log  $K_{-1}$  (1000 K) = -15.63).<sup>1</sup> This channel is invisible to our experiments. Reaction 2 consists of the addition of H atom to the central carbon atom with subsequent displacement of the methyl moiety to produce ethylene. This is actually a chemically activated decomposition. The thermochemistry favors the methyl displacement process overwhelmingly. Thus the measured rate constant refers to the addition process.

H-atom abstraction reactions can take place in three different ways, abstraction of allylic H (reaction 3), vinylic H (reaction 4), and methylvinylic H (reaction 5). Reaction 3 is a source of allyl radicals. A possible sink for allyl radicals in our experiments is their recombination reaction to form 1,5-hexadiene and their reaction with methyl radicals to form 1-butene. Reactions 4 and 5 produce 1- and 2-propenyl radicals. 1-Propenyl radicals decompose into acetylene and methyl radical, while the decomposition of 2-propenyl radicals favors the propyne + H channel. These channels are thermodynamically less favorable than the abstraction of an allylic H-atom.

Received:	December 2, 2010
Revised:	February 18, 2011
Published:	March 15, 2011

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#### Scheme 1

terminal  
addition  
H<sub>3</sub>C — C  
H = CH<sub>2</sub> 
$$\stackrel{\text{terminal}}{\longrightarrow}$$
 H<sub>3</sub>C — C  
H = CH<sub>2</sub>  $\stackrel{\text{terminal}}{\longrightarrow}$  H<sub>3</sub>C — CH<sub>3</sub> (1, -1)  
non-terminal displacement  
addition  
H<sub>3</sub>C — C  $\stackrel{\text{c}}{\longrightarrow}$  CH<sub>2</sub>  $\stackrel{\text{c}}{\longrightarrow}$ 

In a recent study we have examined the analogous reaction mechanism for H-atom reaction with propyne.<sup>2</sup> This furnishes an interesting basis for comparison, involving the effect of the degree unsaturation on nonterminal addition and the consequence for abstraction in going from a propargyl-H to an allylic-H.

The available literature data on the reaction of H atoms with propene and other relevant unsaturated hydrocarbons are compiled in Table 1. Arrhenius parameters have been measured for the overall reaction at temperatures of 298-445 K, resulting in the rate expression of  $1.32 \times 10^{13} \exp(-785/T) \text{ cm}^3/(\text{mol}\cdot\text{s})^3$ and at temperatures of 177-473 K leading to a rate expression of  $6.13 \times 10^{12} \exp(-609/T) \text{ cm}^3/(\text{mol} \cdot \text{s})$ .<sup>4</sup> These are mostly due to terminal addition. Little work has been done at room temperature.<sup>5</sup> Estimates on the ratio of rate constants of nonterminal versus terminal H atom addition have been made at room temperature.<sup>6</sup> The rate constant available for abstraction is an estimate. Particularly important is the absence of direct measurements of the individual rate constants for hydrogen atom attack on propene. A direct measure of methyl displacement and allyl formation may be of particular importance in simulation studies due to the difference in reactivity of these two radicals. The present study is carried out with this aim in mind. It will also lead to a better basis of estimates of related reaction processes.

#### EXPERIMENTAL METHODS

Experiments were carried out in a heated single pulsed shock tube. Details of the apparatus and general procedures have been previously published.<sup>7</sup> For the present purposes, it can be regarded as a pulse reactor with heating time, derived from recorded pressure traces, of 500  $\mu$ s. The unique features of the instrument are the generation of high temperatures and short

residence times, leading to the possibility of studying primary chemical processes, assuring the absence of surface reactions, and minimizing contributions from chain reactions and secondary chemistry. (Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation of endorsement by the National Institute of Standard and Technology, nor does it imply that the material or equipment is necessarily the best available for the purpose.)

Table 2 contains a listing of the mixtures used in these studies along with the temperature and pressure conditions achieved with each. Note particularly the large difference in concentration between the radical source and the target molecules. This guarantees that radicals will not attack radical source or reaction products. Two sources are used to generate H atoms. One of them is hexamethylethane (HME,  $(CH_3)_3C-C(CH_3)_3$ ). Its thermal decomposition takes place via, HME  $\rightarrow$  2 *t*-butyl  $\rightarrow$ 2  $i-C_4H_8 + 2H$ . The reaction is monitored by the disappearance of HME and the formation of *i*-butene. The *i*-butene concentration is a measure of the number of H atoms released into the system. The extent of the reaction of HME decomposition is also used to determine the temperature of the experiment by means of its rate expression  $k(\text{HME} \rightarrow 2 \text{ t-butyl}) = 10^{16.40} \exp(-34400/T) \text{ s}^{-1.8}$ To cover lower temperature regions, experiments have been carried out using t-butylperoxide (tBPO, (CH<sub>3</sub>)<sub>3</sub>CO-OC- $(CH_3)_3$  in an excess of  $H_2$  ( $\approx 20\%$ ) to generate H atom,  $(CH_3)_3CO-OC(CH_3)_3 \rightarrow 2(CH_3)_3CO \rightarrow 2CH_3C(O)CH_3 +$  $2CH_3$ ,  $2CH_3 + 2H_2 \rightarrow 2CH_4 + 2H$ . In this system, chlorocyclopentane is used as a temperature standard. The thermal decomposition of chlorocyclopentane into cyclopentene and hydrogen chloride is characterized by the rate expression  $4.47 \times 10^{13} \exp(-24570/T) \text{ s}^{-1.9}$  Experimental pressures are calculated from the temperature and mixture composition,

#### Table 1. Summary of Relevant Data on the Reaction of Hydrogen Atoms with Alkenes and Alkynes

reaction	rate constant, $cm^3/(mol \cdot s)$	T (K)	P (bar)	reference		
Addition						
$H + propene \rightarrow products$	$1.33 \times 10^{13} \exp(-785/T)$	298-445	0.067	Harris et al. $(1982)^3$		
$H + \text{propend} \rightarrow i-C_2H_7$	$6.13 \times 10^{12} \exp(-609/T)$	177-473	0.067	Kurvlo et al. $(1971)^4$		
· · · · · · · · · · · · · · · · · · ·	$5.3 \times 10^{11}$	298	$1.01 \times 10^{5}$	Munk et al. (1986) <sup>5</sup>		
	$1.32 \times 10^{13} \exp(-785/T)$	300-2500	~	Tsang, W. (1991, 1992) <sup>16,17,a</sup>		
	$5.70 \times 10^9 T^{1.16} \exp(-440/T)$	177-910	133-1200	Seakins et al. $(1993)^1$		
	$9.33 \times 10^{11}$	298	~	Kerr et al. (1972) <sup>12,a</sup>		
$H + propene \rightarrow n-C_3H_7$	$1.32 \times 10^{13} \exp(-1641/T)$	500-2500	~	Tsang, W. (1991, 1992) <sup>16,17a</sup>		
	$5.50 \times 10^{10}$	298	~	Kerr et al. $(1972)^{12,a}$		
$H + propene \rightarrow n-C_3H_7 \rightarrow CH_3 + H_2C=CH_2$	$4.8 \times 10^{13} \exp(-2081/T)$	922-1080	1.7-3.4	this work		
$H + H_2C = CH_2 \rightarrow {}^{\bullet}C_2H_5$	$2.64 \times 10^{13} \exp(-1087/T)$	285-604	0.06-0.8	Lightfoot et al. (1987) <sup>19</sup>		
$H + CH_3CH_2CH = CH_2 \rightarrow i$ -butyl	$8.13  imes 10^{11}$	298	~	Kerr et al. (1972) <sup>12,a</sup>		
$H + CH_3CH_2CH = CH_2 \rightarrow n$ -butyl	$5.01 \times 10^{10}$	298	$\infty$	Kerr et al. (1972) <sup>12,a</sup>		
$H + cis-CH_3CH = CHCH_3 \rightarrow sec-C_4H_9$	$1.61 \times 10^{13} \exp(-965/T)$	200-500	0.799	Kyogoku et al. (1983) <sup>20</sup>		
$H + trans-CH_3CH = CHCH_3 \rightarrow sec-C_4H_9$	$2.39 \times 10^{13} \exp(-1060/T)$	200-500	0.799	Kyogoku et al. (1983) <sup>20</sup>		
$H + CH_3C \equiv CH \rightarrow 1$ -propenyl $\rightarrow C_2H_2 + CH_3$	$6.26 \times 10^{13} \exp(-2267/T)$	889-1068	1.6-7.6	Rosado-Reyes et al. (2010) <sup>2</sup>		
Abstraction						
$H + propene \rightarrow products + H_2$	$6.4 \times 10^{13} \exp(-4168/T)$	1061-1200	1.7-3.4	this work		
$H + propene \rightarrow allyl + H_2$	$1.7 \times 10^5 T^{2.5} \exp(-1254/T)$	500-2500	~	Tsang, W. (1991, 1992) <sup>16,17,a</sup>		
$H + propene \rightarrow 2$ -propenyl + $H_2$	$7.8 \times 10^5 T^{2.5} \exp(-6182/T)$	500-2500	~	Tsang, W. (1991, 1992) <sup>16,17,a</sup>		
$H + propene \rightarrow 1$ -propenyl + $H_2$	$3.9 \times 10^5 T^{2.5} \exp(-2929/T)$	500-2500	~	Tsang, W. (1991, 1992) <sup>16,17,a</sup>		
<sup>a</sup> Data Evaluation.				-		

Table 2. List of Mixtures Used

mixture	components <sup>a</sup>	<i>T</i> (K)	P (bar)
А	4500 ppm propene, 4500 ppm 135TMB, 100 ppm HME, 75 ppm CCP	922-1080	1.6-2.3
В	4066 ppm propene, 3996 ppm propyne, 100 ppm CCP, 50 ppm tBPO, 23% $\rm H_2$	902-1036	1.5-1.9
С	3900 ppm propene, 195 ppm HME	1061-1200	2.4-3.4
<sup><i>a</i></sup> Key: CCP = chlore	ocyclopentane; 135TMB = 1,3,5-trimethylbenzene; tBPO = <i>t</i> -butylperoxide; HME =	hexamethylethane (Note: 1	% = 10000 ppm).

assuming ideal gas properties using the standard shock relations, and no boundary layer or vibrational relaxation effects.

The rate constants for the reaction of H atoms were determined here in comparison with that of H-atom attack on 1,3,5-trimethylbenzene (135TMB, 1,3,5-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>3</sub>) to form *m*-xylene. The process is, H + 1,3,5-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>3</sub>  $\rightarrow$  1,3-(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> + CH<sub>3</sub>. The rate expression for this reaction has been previously determined, *k*(950 to 1100 K) = 6.7 × 10<sup>13</sup> exp(-3255/ *T*) cm<sup>3</sup>/(mol·s).<sup>10</sup> An additional role of 135TMB is that of a radical scavenger to minimize chain processes.

All hydrocarbon samples were from Aldrich Chemicals and were used without purification. Only allene was found as a significant impurity in propyne samples, which was subtracted from the products formed from the course of the reaction. Reaction mixtures were allowed to mix for at least 24 h prior to analysis.

Gas chromatography (Hewlett-Packard 6890N GC), with two chromatographic columns, was used for the product analysis of the reaction mixtures. Light organics  $(C_1-C_4)$  were separated on a 50 m, 0.53 mm i.d., 6.0  $\mu$ m RT-Alumina PLOT column. An advantage from using this column was the successful signal separation of *i*-butene and 1-butene. This was difficult to do in the past and was the reason that H + propene had not yet been studied. Heavier species were separated using a J&W Scientific DB-1 30 m, 0.53 mm i.d., 5% phenylmethylsiloxane (fused silica capillary) column. Once eluted, the detection and quantification of the components were made by flame ionization and mass spectrometry (Agilent Technologies 5973 inert mass selective detector) detection. The GC oven temperature was programmed from -60 to 180 °C.

Retention times and FID response factors of species under analysis were determined from samples of pure compounds. Peak areas were determined using HP ChemStation software and converted to molar quantities based on the experimentally determined response factors.

## RESULTS

**Product Distribution.** The important products that were observed in the after-shock propene mixtures are ethylene, 1-butene, and *i*-butene. *i*-Butene is the result of the decomposition of HME, while the rest of the products come from hydrogen atom attack on propene. Ethylene is the primary product from H addition on propene. When allyl radical, produced from the H allylic abstraction, recombines with methyl radicals, 1-butene is obtained. Other products observed are methane, ethane, acetylene, propyne, and 1,5-hexadiene. Methane originates from methyl radicals from methyl radicals are methyl radicals.



Figure 1. Rate plot for methyl displacement by atomic hydrogen from propene relative to that of 1,3,5-trimethylbenzene.

recombination. Acetylene, propyne, and 1,5-hexadiene are minor products and will not be treated in the present analysis. 1,5-Hexadiene is produced from the allyl + allyl recombination, while acetylene and propyne can be formed from a variety of processes. When 135TMB is added to the mixtures *m*-xylene is found. When tBPO is added to the system, acetone, the large organic decomposition product, is formed. In the presence of chlorocyclopentane, cyclopentene is produced. The relative amounts of methane and ethane that are formed are dependent on the nature of the mixture studied. Another product observed in smaller concentrations is 1,3-dimethyl-5-ethylbenzene, resulting from methyl recombination reactions with dimethylbenzyl, where the latter species is formed by H abstraction in the H + 135TMB reaction.

**Nonterminal Addition and Methyl Displacement.** A direct measure of the relative rate of methyl displacement from propene and 135TMB is obtained by comparing the yields of *m*-xylene and ethylene, normalized for initial concentration of the target molecules or

$$k_{\rm H + propene}/k_{\rm H + 135TMB}$$
  
= [ethylene][135TMB]<sub>i</sub>/[*m*-xylene][propene]<sub>i</sub>

Figure 1 shows an Arrhenius plot of  $k_{H+propene}/k_{H+135TMB}$ , the relative rate constant, for displacement of methyl radical from propene and 1,3,5-trimethylbenzene. The following relative rate expression was obtained

$$\log \frac{k(H + \text{propyne} \rightarrow \text{ethylene} + CH_3)}{k(H + 135\text{TMB} \rightarrow m\text{-xylene} + CH_3)} = (509.58 \pm 68)\frac{1}{T} - (0.144 \pm 0.067); (922 - 1080 \text{ K})$$

The uncertainties listed above are  $\pm \sigma$ . Experimental uncertainties in comparative-rate single-pulse shock tube studies, mostly systematic in nature, have been previously discussed.<sup>11</sup> On the basis of the experimental technique, we estimate that the relative rate constants should be accurate to within  $\pm 10\%$ , while the estimated uncertainty in the relative activation energies is approximately 5 kJ/mol. Relative to the standard reaction of displacement

of methyl from 135TMB, for which  $k_{\text{H}+135\text{TMB}} = 6.7 \times 10^{13} \text{exp} (-3255/T) \text{ cm}^3/(\text{mol}\cdot\text{s})$ , we obtain

$$k(H + \text{propene} \rightarrow \text{ethylene} + CH_3)$$
  
= 4.8 × 10<sup>13</sup> exp( - 2081/T)cm<sup>3</sup>/(mol·s); (922-1080 K)

The methyl displacement channels during the reactions of H + propene and H + propyne are compared to each other in a comparative relative rate experiment. The results are shown in Figure 2, where the yields of acetylene are compared to those of ethylene. For the reaction of methyl displacement by H atoms, the rate constant for the reaction with propene is a factor of 1.05  $\pm$  0.1 larger than that for propyne, as determined from fitting the experimental results

$$\log \frac{k(H + \text{propyne} \rightarrow \text{acetylene} + \text{CH}_3)}{k(H + \text{propene} \rightarrow \text{ethylene} + \text{CH}_3)}$$
  
=  $(-0.461 \pm 0.041) \frac{1000}{T} + (-0.44 \pm 0.04); (902-1036 \text{ K})$ 

Abstraction of H Atoms. Information about the H atom abstraction channels was obtained on the basis of being able to count H atoms in experiments conducted without added inhibitor (mixture C). To recall, a direct measure of the H atoms released in our experiments is the molar concentration of *i*-butene. Assuming that all H atoms produced react with propene via reactions 1-5(Scheme 1), the ethylene formed represents displacement of methyl by H atoms and the difference between the concentrations of *i*-butene and ethylene represents the H-atoms that have disappeared from the system via abstraction reactions. This leads to

$$k(abstraction) = \left(1 - \frac{[ethylene]}{[i-butene]}\right)k(displacement)$$

An Arrhenius plot of the rate constant determined on this basis is shown in Figure 3; it corresponds to a composite value for abstraction of hydrogen from propene by H atoms via reactions



Figure 2. Temperature dependence of rate constant for methyl displacement by atomic hydrogen from propyne relative to that of propene.



Figure 3. Arrhenius plot of the rate constant for the abstraction of H atoms from propene by H atoms.

3, 4, and 5. From the previously determined rate expression for nonterminal addition (above), the temperature-dependent rate expression for hydrogen abstraction is determined to be

$$k(\text{H abstraction}) = 6.4 \times 10^{13} \exp(-4168/T) \text{cm}^3/(\text{mol} \cdot \text{s});$$

$$(1061 - 1200 \text{ K})$$

The possible contribution of propene pyrolysis to the H atom reservoir in the experiments was checked by shocking propene in the absence of hexamethylethane, in a mixture of 0.45% propene and 0.0075% CCP. Ethylene was observed as a product, but its yield was less than 0.01% of the initial propene concentration at the highest temperature.

The yields of ethylene are plotted against those of *i*-butene to obtain information about the branching ratio of H atom nonterminal addition to abstraction (Figure 4). An uncertainty of 2-3% for each concentration measurement is estimated. The data show that H addition takes place  $\approx 81\%$  of the time during the H + propene reaction, while  $\approx 19\%$  corresponds to H abstraction.

# DISCUSSION

Of particular importance is the vast difference in concentrations between the radical source and the target molecule. This guarantees that the radicals that are generated, in particular the H-atoms, will only attack the target molecule. The two radical products from H-atom attack are methyl and allyl. Here again their concentration is much smaller than that of the target molecule. It is also important to notice the high reactivity of H-atoms toward propene and the large rates of



Figure 4. Branching ratio information; ethylene yield vs *i*-butene yield.



**Figure 5.** Comparison of relevant data pertaining to H atom addition reactions. (\*Data evaluation.)

combination of the radicals that are formed. The consequence is that H-atom attack on propene is the only reaction that can occur. Note that the radicals formed cannot add to the unsaturated compounds since under the high temperature conditions the reactions are reversed. This is validated, through carrying out reactions with a variety of substrates and differences in substrate to target molecule concentrations, by the invariance of the results. The general procedure has been employed and similarly validated for studies on similar systems (2, 10, 13, 14). Since all measurements are based on internal standards, small discrepancies in concentrations are significant in terms of uncertainty in the results.

The rate constant for nonterminal H addition on propene has been determined relative to the analogous reaction on H + 135TMB. The rate constant for the reaction of H + propene  $\rightarrow$ ethylene + CH<sub>3</sub> is two times faster than the H + 135TMB  $\rightarrow$  *m*xylene + CH<sub>3</sub> reaction. On a per-methyl basis the results show that H atoms displace methyl radicals from propene 6 times faster



Figure 6. Comparison of reported rate constant expression of H-atom abstraction by atomic hydrogen on a per H-atom basis.

Table 3.	Summary	of Data	Pertaining	to Re	levant H	H A	bstraction	Reactions
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reaction	$k,  \mathrm{cm}^3/(\mathrm{mol}\cdot\mathrm{s})$	<i>k</i> (1000 K)	<i>k</i> per H atom (1000 K)	reference
H + 1,3,5-TMB (9H) $H + toluene (3H)$ $H + isobutene (6H)$ $H + propyne (3H)$	$3.7 \times 10^{14} \exp(-4342/T)$ $1.2 \times 10^{14} \exp(-4138/T)$ $1.7 \times 10^{14} \exp(-4024/T)$ $1.2 \times 10^{14} \exp(-4940/T)$	$\begin{array}{c} 4.81 \times 10^{12} \\ 1.91 \times 10^{12} \\ 3.04 \times 10^{12} \\ 8.59 \times 10^{11} \end{array}$	$5.35 \times 10^{11}$ $6.38 \times 10^{11}$ $5.07 \times 10^{11}$ $2.86 \times 10^{11}$	Tsang et al. (1990) <sup>10</sup> Robaugh et al. (1986) <sup>13</sup> Tsang et al. (1988) <sup>14</sup> Rosado-Reyes et al. (2010) <sup>2</sup>
H + propane (6H) H + propene (3H)	$2.5 \times 10^{12} (T/298 \text{ K})^{2.54} \exp(-3400/T)$ 6.4 × 10 <sup>13</sup> exp(-4168/T)	$1.81 \times 10^{12}$ $9.91 \times 10^{11}$	$3.01  imes 10^{11}$ $3.30  imes 10^{11}$	Tsang (1988) <sup>15</sup> this work

than from 135TMB. The ratio of available sites is however 6 or 3 to 1 in favor of the aromatic compound. It is clear that on a numerical basis H-atom addition, at this temperature, to the olefin may be as much as 12 or 6 times larger per site. The large difference is attributed to the barrier arising from the breaking of the resonance energy of the aromatic ring into a cyclohexadiene structure, indicative of the greater stability of aromatic structures.

The relative rate studies between propene and propyne showed that, for displacement of methyl radical, the reaction of H + propyne (Figure 2). This relative rate ratio is compared to the same ratio taken from the individual rate expressions determinations for both reactions,  $k(C_3H_6 + H, \text{ this work}) = 4.8 \times 10^{13} \exp(-2081/T) \text{ cm}^3/(\text{mol} \cdot \text{s})$ , and  $(C_3H_4 + H, \text{ ref } 2) = 6.3 \times 10^{13} \exp(-2267/T) \text{ cm}^3/(\text{mol} \cdot \text{s})$ . The comparison of the individual determinations shows the contrary; that the reaction of H + propyne is faster by a factor of 1.08. The discrepancy is approximately 13%. This is slightly larger than the 5–10% discrepancy that we would have expected from our analysis of the uncertainties. It may however be a more realistic value.

Table 1 and Figure 5 provide comparisons of relevant rate constants for H atom addition to the terminal and nonterminal positions of C<sub>2</sub> to C<sub>4</sub> species. The existing data on low temperature terminal addition appear to be well established. Our experimental rate constant determination of  $4.8 \times 10^{13} \exp(-2081/T)$ 

for nonterminal H atom addition to propene, when extrapolated to room temperature, differs by  $\approx 240\%$  to the recommended value of  $5.5 \times 10^{10}$  cm<sup>3</sup>/(mol·s) of Kerr et al.<sup>12</sup> It is interesting that the differences between terminal and nonterminal addition decreases as the temperature is increased. Thus differences in rate constants are largely due to those in the activation energy.

Our overall rate constant for H abstraction,  $H + propene \rightarrow$ products + H<sub>2</sub>, is compared with other relevant abstraction rate constants<sup>2,10,13-15</sup> on a per H-atom basis in Figure 6. The data are summarized in Table 3. Our determination of the H abstraction rate expression for the reaction of H + propene of 4.9  $\times$  $10^{13} \exp(-4033/T)$  is comparable to that of propyne within 15% and to that of propane within 10% at 1000 K. Even more surprising is the small difference in rate constants between propane and the two unsaturated compounds. This is contradictory for example to the lower resonance energy of propargyl compared to that of allyl of about 12 kJ/mol. The resonance energy is not manifested in the rate constant during abstraction, in contrast to the breaking of a resonance stabilized bond. One does note the apparently larger rate parameters for propane. This larger activation energy is compensated by a larger A-factor, which is expected. This recommended rate expression for H + propane is however based on an extrapolation from low temperature measurements.

It is interesting that the ratio for methyl and allyl formation from this study is a factor of 4 higher from the recommended values by Tsang,<sup>16,17</sup> estimated on the basis of existing data at lower temperatures. This is due to errors (not unreasonable) of factors of 2 in opposite directions and emphasizes the importance of direct determinations. The experimentally determined ratio of rate expressions is

$$\frac{k(H + \text{propene} \rightarrow n \text{-} \text{propyl}) \rightarrow CH_3 + C_2H_4)}{k(H + \text{propene} \rightarrow H_2 + \text{allyl})}$$
$$= 0.75 \exp(2087/T)$$

This can be compared with the similar ratio of rate expressions for toluene or

$$\frac{k(\mathrm{H} + \mathrm{toluene} \rightarrow \mathrm{methylcyclohexadienyl} \rightarrow \mathrm{CH}_3 + \mathrm{benzene})}{k(\mathrm{H} + \mathrm{toluene} \rightarrow \mathrm{H}_2 + \mathrm{benzyl})}$$
$$= 0.100 \exp(1560/T)$$

Comparisons of these ratios demonstrate that the branching ratio favors benzyl as opposed to allyl formation. This is indicative of the greater inhibitory powers of toluene as compared to propene through more efficient scavenging of H atoms.

During the experiments, yields of acetylene and propyne were observed in small traces and did not provide means to reliably determine the source of these compounds and experimental rate expression for the abstraction of the vinylic and methylvinylic hydrogens in propene. The acetylene yields in our experiments led to a H-vinylic abstraction rate constant that is larger by a factor of 6 (per H atom basis) than that estimated by Knyazev et al.<sup>18</sup> for the analogous reaction of ethylene + H. A possible mechanism involves H atom reaction with allyl radical leading to H + allyl  $\rightarrow$  propene\*  $\rightarrow$  CH<sub>3</sub> + C<sub>2</sub>H<sub>3</sub>  $\rightarrow$  HC=CH + H via a chemically activated process. Due to the complication of the sequence of reactions involving allyl radical, it is not possible to quantitatively examine this possibility in our system.

## SUMMARY AND CONCLUSION

This study presents kinetic and mechanistic information on the H-atom attack on propene. We are deriving the general rules covering abstraction and displacement processes of reactions of H atoms in high-temperature combustion systems. These studies demonstrate little effect of resonance stabilization on the rate constant for removing an H atom by an H atom. We have also found the effect of aromatic versus olefinic and acetylenic structures on the addition of H atoms thus should provide a basis for the estimation of hydrogen atom's reactivity to other unsaturated systems.

# ASSOCIATED CONTENT

**Supporting Information**. Product data and conditions of individual experiments (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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