# **Thermal Decomposition of 1-Butyne in Shock Waves**

YOSHIAKI HIDAKA,\*<sup>,†</sup> TETSUO HIGASHIHARA,\*<sup>,‡</sup> TAKASHI OKI<sup>†</sup>, and HIROYUKI KAWANO<sup>†</sup>

Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790, Japan, and Matsue College of Technology, Nishiikuma-cho, Matsue 690, Japan

## Abstract

1-Butyne diluted with Ar was heated behind reflected shock waves over the temperature range of 1100-1600 K and the total density range of  $1.36 \times 10^{-5} - 1.75 \times 10^{-5}$  mol/cm<sup>3</sup>. Reaction products were analyzed by gas-chromatography. The progress of the reaction was followed by IR laser kinetic absorption spectroscopy. The products were CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, allene, propyne, C<sub>4</sub>H<sub>2</sub>, vinylacetylene, 1,2-butadiene, 1,3-butadiene, and benzene. The present data were successfully modeled with a 80 reaction mechanism. 1-Butyne was found to isomerize to 1,2-butadiene. The initial decomposition was dominated by 1-butyne  $\rightarrow$  C<sub>3</sub>H<sub>3</sub> + CH<sub>3</sub> under these conditions. Rate constant expressions were derived for the decomposition to be  $k_7 = 3.0 \times 10^{15} \exp(-75800 \text{ cal/}RT) \text{ s}^{-1}$  and for the isomerization to be  $k_4 = 2.5 \times 10^{13} \exp(-65000 \text{ cal/}RT) \text{ s}^{-1}$ . The activation energy 75.8 kcal/mol was cited from literature value and the activation energy 65 kcal/mol was assumed. These rate constant expressions are applicable under the present experimental conditions, 1100-1600 K and 1.23-2.30 atm. © 1995 John Wiley & Sons, Inc.

# Introduction

In a previous article [1], we found that 2-butyne  $(2-C_4H_6)$  rapidly isomerizes to 1,2-butadiene  $(1,2-C_4H_6)$  and 1,3-butadiene  $(1,3-C_4H_6)$  before the decomposition of  $2-C_4H_6$  takes place and proposed rate constants of these isomerizations.

In this study, in order to elucidate the difference of reactivity between 1-butyne  $(1-C_4H_6)$  and  $2-C_4H_6$ , we performed a shock tube experiment on the pyrolysis of  $1-C_4H_6$  using single-pulse and time-resolved IR laser absorption methods. We found that  $1-C_4H_6$  decomposes rapidly to  $C_3H_3$  and  $CH_3$  and that  $1-C_4H_6$  also isomerizes to  $1,2-C_4H_6$ . We will discuss the kinetics of  $1-C_4H_6$  decomposition based on a detailed computer modeling study.

# **Experimental**

Two shock tubes of 4.1-cm i.d. were used in this experiment. The apparatus and procedures were the same as those used previously [1], so a brief description is given here. One is a magic-hole type shock tube. Within 20 s after shock heating, the reacted mixtures were analyzed on three serially connected gas chromatographs. An identification and a quantification of each product were done as before [1]. The other is a standard-type shock tube connected to an IR laser absorption apparatus.

<sup>\*</sup>To whom correspondence should be addressed.

<sup>&</sup>lt;sup>†</sup>Ehime University.

<sup>&</sup>lt;sup>‡</sup> Matsue College of Technology.

International Journal of Chemical Kinetics, Vol. 27, 321–330 (1995) © 1995 John Wiley & Sons, Inc.

The transmitted intensities of a 3.39  $\mu$ m He—Ne laser beam through a 4.1-cm path length in the shock tube and through an interference filter ( $\lambda_{max} = 3.39 \ \mu$ m, halfwidth = 0.072  $\mu$ m) were observed with a Jadson J10D-M204 InSb detector. The 3.39  $\mu$ m laser beam is absorbed by many hydrocarbons. Therefore it is necessary to know decadic molar extinction coefficients for all the products and the reactant in order to compare experimental absorption profiles with computed ones. These values have been measured previously [1]. As is shown later, the 3.39  $\mu$ m laser beam is mainly absorbed by 1-C<sub>4</sub>H<sub>6</sub>, 1,2-C<sub>4</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>6</sub>, and CH<sub>4</sub>.

The test gas composition used here was 1%  $1-C_4H_6$  in Ar. All the experiments were done in reflected shock waves over the temperature range 1100-1600 K. Initial sample pressure was kept at 50 torr, giving reflected shock densities in the range of  $1.36 \times 10^{-5} - 1.75 \times 10^{-5}$  mol/cm<sup>3</sup> (1.23-2.30 atm).

#### Results

#### Data Reduction

The products of the pyrolysis of  $1-C_4H_6$  were  $1,3-C_4H_6, 1,2-C_4H_6$ ,  $CH_4, C_2H_2, C_2H_4, C_2H_6$ , allene (AC<sub>3</sub>H<sub>4</sub>), propyne (PC<sub>3</sub>H<sub>4</sub>), vinylacetylene (C<sub>4</sub>H<sub>4</sub>), diacetylene (C<sub>4</sub>H<sub>2</sub>), and benzene (C<sub>6</sub>H<sub>6</sub>). The yields of these products and remaining  $1-C_4H_6$  were plotted against temperature in Figure 1. The formation of  $2-C_4H_6$  was not observed. 1,2-C<sub>4</sub>H<sub>6</sub>, AC<sub>3</sub>H<sub>4</sub>, C<sub>4</sub>H<sub>4</sub>, and CH<sub>4</sub> were observed at the lowest temperature of the experiment (1100 K). 1,3-C\_4H<sub>6</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>4</sub>H<sub>2</sub>, and C<sub>6</sub>H<sub>6</sub> were observed at higher temperatures than those species mentioned above. This fact means that the decomposition and the isomerization of  $1-C_4H_6$  take place simultaneously.



Figure 1. Single pulse shock tube date (product distribution) for the  $1\% 1-C_4H_6-99\%$  Ar mixture. (-----): computed with the ref. [1] mechanism and (-----): see text. Effective heating times are 2400  $\mu$ s (1100 K), 2240  $\mu$ s (1200 K), 2070  $\mu$ s (1300 K), 1920  $\mu$ s (1400 K), 1750  $\mu$ s (1500 K), and 1590  $\mu$ s (1600 K).



Figure 2. Comparison of experimental  $(\bigcirc)$  with computed (lines) IR laser absorption data,  $A_t$ , at 50  $\mu$ s, 100  $\mu$ s, and 200  $\mu$ s: (----): computed using the ref. [1] mechanism; (-----): computed by multiplying the rate constants  $k_4$  (lower) and  $k_7$  (upper) by 0.2; (----): absorption due to 1-C<sub>4</sub>H<sub>6</sub>, 1,2-C<sub>4</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>6</sub>, and CH<sub>4</sub>.

In order to parameterize the progress of early stage reaction from the IR absorption profiles, we measured  $A_{50}$ ,  $A_{100}$ , and  $A_{200}$  according to the equation  $A_t = \log(I_f/I_t)/\log(I_f/I_0)$ , where  $I_f$  is the transmitted intensity with no absorption, and  $I_0$ and  $I_t$  are the transmitted intensities at the shock front and time t, respectively. These data are plotted against temperature in Figure 2.

#### Modeling Calculation

The mechanism used to interpret the present data is the same as that used in our previous study for the isomerization and decomposition of  $2-C_4H_6$  [1]. As the initial step of the reaction, the isomerization of  $1-C_4H_6$  to  $1,2-C_4H_6$  and the decomposition of  $1-C_4H_6$  to  $C_3H_3$  and  $CH_3$ ,

(4) 
$$1-C_4H_6 = 1, 2-C_4H_6 \quad \Delta H_{298}^\circ = -0.7 \text{ kcal/mol}$$

(7) 
$$1-C_4H_6 = C_3H_3 + CH_3 \quad \Delta H^{\circ}_{298} = 78.3 \text{ kcal/mol},$$

were found to be important. Rate constant of reaction 4 was optimized as follows. The activation energy, 65 kcal/mol, was assumed to be the same as the estimated highest barrier of the lowest energy path of the isomerization (see Scheme I), and the preexponential factor was varied so as to reproduce the experimental data. The best expression was  $k_4 = 2.5 \times 10^{13} \exp(-65000 \text{ cal/}RT) \text{ s}^{-1}$ . Rate constant of reaction 7 was derived as follows. As there are no experimental rate data for reaction 7, we initially adopted the high pressure limit rate constant,  $k_{7,\infty} = 5.0 \times 10^{15} \exp(-75800 \text{ cal/}RT) \text{ s}^{-1}$ , which was estimated by Dean [2]. Using this high pressure limit rate constant, our experimental results could be reproduced fairly well. In order to obtain better agreement, we varied A factor of the above expression Ea remaining unchanged. The best agreement was achieved by using the expression  $k_7 = 3.0 \times 10^{15} \exp(-75800 \text{ cal/}RT) \text{ s}^{-1}$ . The expression is very close to the expression  $k_7 = 3.5 \times 10^{15} \exp(-74500 \text{ cal/}RT) \text{ s}^{-1}$ , which is estimated by Tsang [3,4].



The C—H bond fission of  $1-C_4H_6$ ,

(a1) 
$$1-C_4H_6 = 1-IC_4H_5 + H \quad \Delta H_{298}^\circ = 86.6 \text{ kcal/mol}$$
  
 $k_{a1} = 6.3 \times 10^{14} \exp(-86000 \text{ cal/}RT) \text{ s}^{-1} \text{ (assumed)},$ 

had negligible effect on the computed results, as long as we used the rate constant given above, where 1-IC<sub>4</sub>H<sub>5</sub> represents resonant stabilized radical,  $CH \equiv C-CH-CH_3 \leftrightarrow CH = C = CH-CH_3$ . The  $k_{a1}$  expression is derived as follows. The preexponential factor,  $6.3 \times 10^{14} \text{ s}^{-1}$ , is assumed to be the same as that for the similar reaction,  $CH_2 = CH-CH_2-CH_3 \rightarrow CH_2 = CH-CH_3 + H$ , which rate is estimated by Dean [2] to be  $k_{\infty} = 6.3 \times 10^{14} \exp(-82400 \operatorname{cal}/RT) \operatorname{s}^{-1} (\Delta H_{298}^{\circ} = 82.5 \operatorname{kcal/mol})$ . The activation energy, 86 kcal/mol, is assumed to be nearly equal to the heat of reaction.

Solid lines in Figures 1 and 2 are the results computed using the mechanism of Table I in ref. [1] (hereafter denoted as the ref. [1] mechanism). As are seen in these figures, the present data are satisfactorily modeled by the ref. [1] mechanism and the rate constant set. The solid lines (computed  $A_t$  values) in Figure 2 are the sum of the absorption by the reactant and many products. At low temperatures, however, the 3.39  $\mu$ m laser beam is mainly absorbed by 1-C<sub>4</sub>H<sub>6</sub>, and the  $A_t$  values are a good measure of the consumption rate of 1-C<sub>4</sub>H<sub>6</sub>. At high temperatures, many products (especially 1,2-C<sub>4</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>6</sub>, and CH<sub>4</sub>) contribute to the absorption.

We calculated the pR values [5] (logarithms of absolute values of net reaction rates in molecules cm<sup>-3</sup>s<sup>-1</sup> units) at 1300 K using the ref. [1] mechanism. In Table I, we listed the reactions whose rates are 1% or more of the rate of the fastest one. There are a lot of pressure dependent reactions. It should be noted that the rate constant expressions assigned for these reactions are applicable under the present experimental conditions, 1100–1600 K and 1.23–2.30 atm. In Figure 3, the pR values at 1300 K against time are shown for the reactions whose rate are 5% or more of the rate of the fastest one (A is for the consumption of 1-C<sub>4</sub>H<sub>6</sub> and B is for others). As is seen in this figure, 1-C<sub>4</sub>H<sub>6</sub> is mainly consumed by reactions 4 and 7. These reactions are competing ones and the branching ratio  $k_4/k_7$ , which can reproduce the present data, is about 3/5 at 1300 K. The following reactions are also important to the consumption of 1-C<sub>4</sub>H<sub>6</sub>: H atom addition to 1-C<sub>4</sub>H<sub>6</sub> and subsequent decomposition of the adduct to AC<sub>3</sub>H<sub>3</sub> and CH<sub>3</sub> (reaction 13) or to C<sub>2</sub>H<sub>5</sub> and C<sub>2</sub>H<sub>2</sub> (reaction 14); abstraction of H atom from 1-C<sub>4</sub>H<sub>6</sub> by H (reactions 19 and 20) and by CH<sub>3</sub> (reactions 25 and 26).

	Reaction	A	n	Ea	Ref.
1	$2 - C_4 H_6 = 1, 3 - C_4 H_6$	3.00E + 13	0.0	65.0	с
2	$2 - C_4 H_6 = 1, 2 - C_4 H_6$	3.00E + 13	0.0	67.0	с
3	$1,2-C_4H_6 = 1,3-C_4H_6$	2.50E + 13	0.0	63.0	[15]
4	$1-C_4H_6 = 1,2-C_4H_5$	2.50E + 13	0.0	65.0	this work
6	$1,2-C_4H_6 = C_3H_3 + CH_3$	2.00E + 15	0.0	75.0	[15]
7	$1 - C_4 H_6 = C_3 H_3 + C H_3$	3.00E + 15	0.0	75.8	this work
10	$2 - C_4 H_6 + H = C H_3 + P C_3 H_4$	2.60E + 05	2.5	1.0	с
11	$1,3-C_4H_6 + H = C_2H_3 + C_2H_4$	4.00E + 13	0.0	5.0	[14]
12	$1,2-C_4H_6 + H = CH_3 + AC_3H_4$	6.00E + 12	0.0	2.1	с
13	$1-C_4H_6 + H = CH_3 + AC_3H_4$	1.30E + 05	2.5	1.0	assumed
14	$1 - C_4 H_6 + H = C_2 H_5 + C_2 H_2$	6.50E + 04	2.5	1.0	adjusted
18	$1,2-C_4H_6 + H = 1,2-C_4H_5 + H_2$	6.50E + 13	0.0	9.4	с
19	$1-C_4H_6 + H = 1-IC_4H_5 + H_2$	6.50E + 13	0.0	9.4	assumed
20	$1 - C_4 H_6 + H = 1 - N C_4 H_5 + H_2$	6.50E + 13	0.0	9.4	assumed
22	$1,3-C_4H_6 + CH_3 = 1,3-NC_4H_5 + CH_4$	4.00E + 14	0.0	22.8	с
<b>24</b>	$1,2-C_4H_6 + CH_3 = 1,2-C_4H_5 + CH_4$	1.00E + 14	0.0	19.5	с
25	$1-C_4H_6 + CH_3 = 1-IC_4H_5 + CH_4$	1.00E + 14	0.0	19.5	assumed
<b>26</b>	$1 - C_4 H_6 + C H_3 = 1 - N C_4 H_5 + C H_4$	1.00E + 14	0.0	19.5	assumed
37	$1,3-NC_4H_5 = C_2H_3 + C_2H_2$	1.00E + 14	0.0	43.9	[14]
38	$H + C_4 H_4 = 1,3-NC_4 H_5$	2.00E + 13	0.0	3.0	[14]
39	$1,2-C_4H_5 = C_4H_4 + H$	3.00E + 13	0.0	45.0	с
40	$1 - IC_4H_5 = C_4H_4 + H$	3.00E + 13	0.0	45.0	assumed
41	$1 - NC_4H_5 = C_4H_4 + H$	3.00E + 13	0.0	45.0	assumed
<b>42</b>	$1-NC_4H_5 = C_2H + C_2H_4$	2.00E + 14	0.0	57.0	c
46	$C_4H_4 + H = C_2H_3 + C_2H_2$	2.00E + 13	0.0	3.6	с
50	$C_2H_2 + C_2H = C_4H_2 + H$	9.03E + 13	0.0	0.0	с
56	$PC_3H_4 + M = C_3H_3 + H + M$	4.70E + 18	0.0	80.0	с
58	$\mathbf{PC}_3\mathbf{H}_4 + \mathbf{H} = \mathbf{C}_2\mathbf{H}_2 + \mathbf{CH}_3$	1.30E + 05	2.5	1.0	с
59	$AC_3H_4 = PC_3H_4$	2.50E + 12	0.0	59.0	с
60	$AC_{3}H_{4} + M = C_{3}H_{3} + H + M$	2.00E + 18	0.0	80.0	с
61	$C_2H_6 = CH_3 + CH_3$	7.00E + 14	0.0	80.0	с
64	$C_2H_6 + H = C_2H_5 + H_2$	1.30E + 14	0.0	9.4	с
66	$C_2H_5 = C_2H_4 + H$	1.20E + 12	0.0	35.0	с
68	$\mathbf{C}_2\mathbf{H}_3 + \mathbf{M} = \mathbf{C}_2\mathbf{H}_2 + \mathbf{H} + \mathbf{M}$	7.90E + 14	0.0	31.5	с
75	$C_3H_3 + C_3H_3 = C_6H_6$	3.00E + 12	0.0	0.0	adjusted
76	$C_3H_3 + C_3H_3 = C_6H_5 + H_5$	1.20E + 14	0.0	10.0	[14]
79	$C_{6}H_{5}\ +\ C_{2}H_{2}\ =\ C_{8}H_{6}\ +\ H$	1.00E + 13	0.0	0.0	с

TABLE I. Important reactions<sup>a</sup> and their rate constant expressions.<sup>b</sup>

<sup>a</sup> The reaction numbering system follows ref. [1].

<sup>b</sup> Rate constants are given in the form,  $k = AT^n \exp(-Ea/RT)$ . The units are cm, mol, kcal, s, and K.

<sup>c</sup> Reference [1] and references cited therein.

From the pR values shown in Figure 3, the routes of the formation of the major products can be elucidated:  $1,3-C_4H_6$  is produced by the isomerization of  $1,2-C_4H_6$  (reaction 3);  $C_4H_4$  by reactions 40 and 41; allene by reaction 13; propyne by reactions 56 and 59;  $C_2H_4$  by reaction 66, where  $C_2H_5$  is mainly produced by reaction 14;  $C_2H_2$  by reaction 14;  $CH_4$  by reactions 25 and 26;  $C_2H_6$  by reaction 61; and  $C_6H_6$  by reaction 75.

Figure 4 shows the sensitivity spectra [5] for the yields of main products and for the remaining  $1-C_4H_6$ , which are determined by multiplying and dividing the rate constant values given in Table I by 5. Not only the remaining  $1-C_4H_6$  but also the



Figure 3. Reaction rate (pR) profiles at 1300 K. (A) is for the consumption of  $1\text{-}C_4H_6$  and (B) is for others.

yields of  $1,2-C_4H_6$ ,  $C_2H_6$ , and  $C_6H_6$  are very sensitive to the rate of reaction 7. The IR absorption data are also sensitive to the rate reaction 7 (see Fig. 2). Thus, reaction 7 is primarily important in the pyrolysis of  $1-C_4H_6$ .

The yield of  $1,2-C_4H_6$  is not so sensitive to the rate of the isomerization of  $1-C_4H_6$  to  $1,2-C_4H_6$  (reaction 4) at 1300 K. Instead, the yield of  $1,3-C_4H_6$  is sensitive to the rate of reaction 4, because the  $1,2-C_4H_6$  formed by reaction 4 isomerizes rapidly to



Figure 4. Logarithmic response sensitivity spectra at 1300 K. The open boxes were computed by multiplying the rate constant values in Table I by 5 and the solid boxes by dividing by 5.

1,3-C<sub>4</sub>H<sub>6</sub> by reaction 3. Below 1300 K, however, the yield of 1,2-C<sub>4</sub>H<sub>6</sub> is sensitive to the rate of reaction 4.

The yields of  $C_2H_4$  and  $C_2H_2$  are sensitive to the rates of reactions 13 and 14, and the yield of  $AC_3H_4$  is sensitive to the rate of reaction 13. Reactions 13 and 14 will proceed as follows:

(13)  

$$H - C \equiv C - C - C - H + H \rightarrow H - C = C - C - H \rightarrow CH_3 + AC_3H_4$$

$$H - C \equiv C - C - C - H \rightarrow CH_3 + AC_3H_4$$

(14)

$$H-C \equiv C \xrightarrow{H} H H H H \longrightarrow H \xrightarrow{H} H H H H$$
  
$$H-C \equiv C \xrightarrow{H} H H H H H \longrightarrow H \xrightarrow{H} C_2 H_5 + C_2 H_2.$$

The rate constant ratio  $k_{13}/k_{14}$ , which could reproduce the yields of C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and AC<sub>3</sub>H<sub>4</sub>, was 2.

#### Discussion

In the previous section, we showed that reaction 7 is primarily important in the pyrolysis of 1-C<sub>4</sub>H<sub>6</sub>. Without this reaction, we could not predict the yields of CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, AC<sub>3</sub>H<sub>4</sub>, PC<sub>3</sub>H<sub>4</sub>, and C<sub>6</sub>H<sub>6</sub>. As is seen in Figure 3, because the rate of reaction 7 is fastest and more than 30% of 1-C<sub>4</sub>H<sub>6</sub> is consumed by this reaction, appreciable amounts of CH<sub>3</sub> and C<sub>3</sub>H<sub>3</sub> are produced. About 50% of CH<sub>3</sub> recombine to produce C<sub>2</sub>H<sub>6</sub>, and about 50% of C<sub>3</sub>H<sub>3</sub> recombine to produce C<sub>6</sub>H<sub>6</sub>. This is the reason why the yields of C<sub>2</sub>H<sub>6</sub> and C<sub>6</sub>H<sub>6</sub> are sensitive to the rate of reaction 7. The proposed rate constant  $k_7 = 3.0 \times 10^{15} \exp(-75800 \operatorname{cal}/RT) \operatorname{s}^{-1}$  is close to the estimated high pressure limit rate constants [2–4], implying that reaction 7 is close to the high pressure limit under the present experimental conditions.

Although  $1,2-C_4H_6$  is partly formed by the recombination of  $C_3H_3$  and  $CH_3$ (reaction -6), most of  $1,2-C_4H_6$  is formed by the isomerization of  $1-C_4H_6$  (reaction 4). Without reaction 4, we could not reproduce not only the yield of  $1,2-C_4H_6$  but also that of  $1,3-C_4H_6$ . The isomerization of  $1-C_4H_6$  to  $1,2-C_4H_6$  is quite similar to the isomerization of propyne to allene, and two paths are possible (see Scheme I). Energy barriers of the isomerization of  $1-C_4H_6$  to  $1,2-C_4H_6$  would be similar to those of the isomerization of propyne to allene, because the  $CH_3$  group in 1-C<sub>4</sub>H<sub>6</sub> is not directly involved in a reaction. Relative energies given in Scheme I are obtained by assuming that the energies of the isomerization  $1-C_4H_6 \rightleftharpoons 1, 2-C_4H_6$  are the same as those of the isomerization propyne  $\rightleftharpoons$  allene obtained by Yoshimine et al. [6,7]. The isomerization via TS1, TS2, 2-methyl-1-cyclopropene, and TS3 (Path I) is easier than the isomerization via TS4 and TS3 (Path II) by 8 kcal/mol. It is therefore preferable that the isomerization of  $1-C_4H_6$  to  $1,2-C_4H_6$  would proceed by the Path I mechanism as suggested by Yoshimine et al. for the isomerization of propyne to allene. It is confirmed by Kakumoto et al. [8] and by Karni et al. [9] that the experimental results for the isomerization between propyne and allene can well be explained by the Path I mechanism. The highest barrier of the Path I is 65 kcal/mol (TS3). We tentatively

HIDAKA ET AL.

adopted 65 kcal/mol as the apparent activation energy of reaction 4. This activation energy can well explain our experimental results, although the present experimental results are not so sensitive to the variation of the apparent activation energy of reaction 4. For example, the activation energy 60 kcal/mol or 70 kcal/mol can also reproduce the present results fairly well, as long as the absolute value of  $k_4$  remains the same at 1400 K.

The reaction,

(a2) 
$$H-C \equiv C \xrightarrow{H} H + H \xrightarrow{H} H + H \xrightarrow{H} H + H$$
$$H \xrightarrow{H} H \xrightarrow{H} C \equiv C \xrightarrow{H} H + H \xrightarrow{H} H \xrightarrow{H} H \xrightarrow{H} H \xrightarrow{H} H$$
$$H \xrightarrow{H} H \xrightarrow{H} H$$

is another possible route for the formation of  $1,2-C_4H_6$  from  $1-C_4H_6$ . Reactions 13 and a2 are competing ones. If the rate constant of reaction a2 is comparable to that of reaction 13, this reaction does contribute to the formation of  $1,2-C_4H_6$ . That is, about 25% of  $1,2-C_4H_6$  becomes to be produced through this reaction at 1300 K. However, the  $CH_2 = \dot{C}-CH_2 - CH_3$  radical would mainly decompose to CH3 and  $AC_3H_4$ , because the C-C bond rupture to produce  $CH_3$  and  $AC_3H_4$  is easier by 10 kcal/mol than the C-H bond rupture to produce  $1,2-C_4H_6$  and H. If the rate constant of reaction a2 is 1/5 or less of that of reaction 13, the effect of reaction a2 on the formation of  $1,2-C_4H_6$ is negligible. At present, we do not include reaction a2 in our mechanism.

We did not include the following isomerizations

(a3) 
$$1-C_4H_6 = 2-C_4H_6$$

(a4) 
$$1-C_4H_6 = 1, 3-C_4H_6$$

in our mechanism. The inclusion of reaction a3 with the rate constant  $k_{a3} = k_4$  predicts applicable amount of 2-C<sub>4</sub>H<sub>6</sub> formation, while we did not observe the formation of 2-C<sub>4</sub>H<sub>6</sub>. The yield of 2-C<sub>4</sub>H<sub>6</sub> computed using the ref. [1] mechanism (without reaction a3) are 0.36% (1200 K), 0.57% (1400 K), and 0.02% (1600 K), supporting the experimental result. The inclusion of reaction a4 with the rate constant  $k_{a4} = k_4$  predicts much more formation of 1,3-C<sub>4</sub>H<sub>6</sub> than that observed (see broken line in Fig. 1). These isomerizations require more complicated H shifts (for example, simultaneous 1,3-H shifts of two H atoms) than that for reaction 4 and would be hard to occur.

The product species observed in the pyrolysis of  $1-C_4H_6$  are the same as those observed in the pyrolysis of  $2-C_4H_6$ . However, the yields of  $1,3-C_4H_6$ ,  $AC_3H_4$ ,  $C_2H_6$ , and  $C_6H_6$  are much different between the pyrolysis of  $1-C_4H_6$  and  $2-C_4H_6$ . As are described below, the ref. [1] mechanism can well predict these differences.

The maximum yield of  $1,3-C_4H_6$  in the pyrolysis of  $2-C_4H_6$  is about 30%, whereas that in the pyrolysis of  $1-C_4H_6$  is about 10%. The reason of this difference is that  $2-C_4H_6$  can directly isomerize to  $1,3-C_4H_6$  (reaction 1) with the rate constant of  $k_1 = 3.0 \times 10^{13} \exp(-65000 \text{ cal/}RT) \text{ s}^{-1}$ , whereas  $1-C_4H_6$  cannot. In the pyrolysis of  $1-C_4H_6$ ,  $1,3-C_4H_6$  is mainly produced through  $1,2-C_4H_6$  (reaction 3).

The maximum yield of  $AC_3H_4$  in the pyrolysis of  $1-C_4H_6$  is 10%, whereas that in the pyrolysis of  $2-C_4H_6$  is 3%. In the pyrolysis of  $1-C_4H_6$ ,  $AC_3H_4$  is mainly produced by the addition of H atom to  $1-C_4H_6$  and subsequent decomposition of the adduct (reaction 13). On the other hand, the adduct of H atom to  $2-C_4H_6$  decomposes to  $CH_3$  and  $PC_3H_4$  (reaction 10).

We observed much more formation of  $C_2H_6$  and  $C_6H_6$  in the pyrolysis of 1- $C_4H_6$  than in the pyrolysis of 2- $C_4H_6$ .  $C_2H_6$  is produced by the recombination of  $CH_3$ , and  $C_6H_6$  by the recombination of  $C_3H_3$ . The yields of  $C_2H_6$  and  $C_6H_6$  are therefore good measure of the formation rates of  $CH_3$  and  $C_3H_3$ . 1- $C_4H_6$  rapidly decomposes to  $CH_3$  and  $C_3H_3$  (reaction 7), whereas 2- $C_4H_6$  initially isomerizes to 1,2- $C_4H_6$  and 1,3- $C_4H_6$ , and only the 1,2- $C_4H_6$  can decompose to  $CH_3$  and  $C_3H_3$ .

In recent years, much attention has been paid to the formation of benzene (or soot) from aliphatic fuels. In the present experiment, we observed that about 15% of initial  $1-C_4H_6$  is converted to benzene at around 1500 K. Our mechanism includes four channels for the formation of  $C_6H_6$  (or  $C_6H_5$ ):

(71)  $1, 3-NC_4H_5 + C_2H_2 = C_6H_6 + H$ 

(72) 
$$NC_4H_3 + C_2H_2 = C_6H_5$$

(75) 
$$C_3H_3 + C_3H_3 = C_6H_6$$

(76) 
$$C_3H_3 + C_3H_3 = C_6H_5 + H$$

Almost all C<sub>6</sub>H<sub>6</sub>, however, is found to be produced through reaction 75, confirming the conclusion of Kern et al. [10], Stein et al. [11], and Miller and Melius [12] that the C<sub>3</sub>H<sub>3</sub>+ C<sub>3</sub>H<sub>3</sub> reaction is a likely source of C<sub>6</sub>H<sub>6</sub>. The proposed rate constant  $k_{75} =$  $3.0 \times 10^{12}$  cm<sup>3</sup>mol<sup>-1</sup>s<sup>-1</sup> is consistent with the values  $k_{75} = 5.0 \times 10^{12}$  cm<sup>3</sup>mol<sup>-1</sup>s<sup>-1</sup> estimated by Organ and Mackie [13],  $k_{75} = 3.16 \times 10^{12}$  cm<sup>3</sup>mol<sup>-1</sup>s<sup>-1</sup> by Stein et al. [11], and  $k_{75} = 10^{12 \pm 0.5}$  cm<sup>3</sup>mol<sup>-1</sup>s<sup>-1</sup> by Tsang [4]. Reaction 75 is not a single reaction. The route of C<sub>6</sub>H<sub>6</sub> formation from C<sub>3</sub>H<sub>3</sub> recombination has been discussed by Stein et al. and by Miller and Melius. In the pyrolysis of 1,3-C<sub>4</sub>H<sub>6</sub> [14], 2-C<sub>4</sub>H<sub>6</sub> [1], and 1,2-C<sub>4</sub>H<sub>6</sub> [15], we observed the formation of benzene and measured the yield of benzene to be about 1.5% (1% 1,3-C<sub>4</sub>H<sub>6</sub>-99% Ar mixture), 4% (2.5% 2-C<sub>4</sub>H<sub>6</sub>-97.5% Ar mixture), and 7% (1% 1,2-C<sub>4</sub>H<sub>6</sub>-99% Ar mixture) at around 1500 K. These yields of benzene can also be reproduced by the ref. [1] mechanism, confirming that benzene is mainly formed by reaction 75.

## **Bibliography**

- [1] Y. Hidaka, T. Higashihara, N. Ninomiya, H. Oshita, and H. Kawano, J. Phys. Chem., 97, 10977 (1993).
- [2] A.M. Dean, J. Phys. Chem., 89, 4600 (1985).
- [3] W. Tsang, Int. J. Chem. Kinet., 2, 23 (1970).
- [4] W. Tsang, Int. J. Chem. Kinet., 10, 687 (1978).
- [5] W.C. Gardiner, Jr., J. Phys. Chem., 81, 2367 (1977).
- [6] N. Honjyou, J. Pacansky, and M. Yoshimine, J. Am. Chem. Soc., 106, 5361 (1984).
- [7] M. Yoshimine, J. Pacansky, and N. Honjyou, J. Am. Chem. Soc., 111, 4189 (1989).
- [8] T. Kakumoto, T. Ushirogouchi, K. Saito, and A. Imamura, J. Phys. Chem., 91, 183 (1987).
- [9] M. Karni, I. Oref, S. Barzilai-Gilboa, and A. Lifshitz, J. Phys. Chem., 92, 6924 (1988).
- [10] (a) R. D. Kern, H. J. Singh, and C. H. Wu, Int. J. Chem. Kinet., 20, 731 (1988); (b) C. H. Wu and R. D. Kern, J. Phys. Chem., 91, 6291 (1987).
- [11] S.E. Stein, J.A. Walker, M.M. Suryan, and A. Fahr, 23rd. Symp. (Int.) on Combustion, The Combustion Institute, Pittsburgh, 1990, p. 85.

- [12] J.A. Miller and C.F. Melius, Combust. Flame, 91, 21 (1992).
- [13] P.P. Organ and J.C. Mackie, J. Chem. Soc. Faraday Trans., 87, 815 (1991).
- [14] Y. Hidaka, T. Higashihara, N. Ninomiya, H. Masaoka, T. Nakamura, and H. Kawano, submitted for publication.
- [15] Y. Hidaka, T. Higashihara, N. Ninomiya, T. Oki, and H. Kawano, Int. J. Chem. Kinet., in press.

Received April 29, 1994 Accepted August 1, 1994