# High Temperature Pyrolysis of 1,5-Cyclooctadiene and 4-Vinylcyclohexene in Shock Waves

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#### Abstract

1,5-cyclooctadiene or 4-vinylcyclohexene mixture diluted with argon was heated to temperatures in the range 880–1230 K behind reflected shock waves. Profiles of IR-laser absorption were measured at 3.39  $\mu$ m. From these profiles, rate constants  $k_1$  and  $k_2$  for the decyclization reactions 1,5-cyclooctadiene  $\rightarrow$  biradical and 4-vinylcyclohexene  $\rightarrow$  biradical were evaluated as  $k_1 = 5.2 \times 10^{14} \exp(-48.3 \text{ kcal}/RT) \text{ s}^{-1}$  and  $k_2 = 3.5 \times 10^{14} \exp(-55.3 \text{ kcal}/RT) \text{ s}^{-1}$ , respectively. © 1993 John Wiley & Sons, Inc.

#### Introduction

The pyrolysises of 1.5-cyclooctadiene  $(cC_8H_{12})$  and 4-vinylcyclohexene  $(vC_8H_{12})$  have been studied by several workers [1-4]. The pyrolysis of 1,5-cyclooctadiene has been shown to produce 4-vinylcyclohexene at low temperatures and also 1,3-butadiene at temperatures above about 600 K [1,2]. It has been considered that the products 4-vinylcyclohexene and 1,3-butadiene come from a common precursor and the only consistent mechanism is one involving the allylic biradical  $(bC_8H_{12})$  [5].

$$cC_8H_{12} \xrightarrow{k_1} bC_8H_{12} \xrightarrow{k_2} vC_8H_{12}$$
  
 $\downarrow k_3$   
 $1,3-C_4H_6 + 1,3-C_4H_6$ 

Srinivasan and Levi [1] reported the rate constant  $2.9 \times 10^{14} \exp(-49 \text{ kcal}/RT) \text{ s}^{-1}$  for the pyrolysis of 1,5-cyclooctadiene over the temperature range of 573-600 K. The rate constants  $3.55 \times 10^{15} \exp(-52.4 \text{ kcal}/RT) \text{ s}^{-1}$  and  $1.99 \times 10^{16} \exp(-55.9 \text{ kcal}/RT) \text{ s}^{-1}$  for the thermal reorganization of 1,5-cyclooctadiene to 4-vinylcyclohexene and 1,3-butadiene were also

International Journal of Chemical Kinetics, Vol. 25, 1037–1042 (1993) © 1993 John Wiley & Sons, Inc. CCC 0538-8066/93/121037-06 reported by Doering et al. [2]. Benson [5] also evaluated  $k_2 = 1.99 \times 10^{14} \exp(-56.7 \text{ kcal/RT}) \text{ s}^{-1}$  from the Doering et al. results [2].

The pyrolysis of 4-vinylcyclohexene was first studied using a singlepulse shock tube by Tsang [3]. He found that the only hydrocarbon fragment observed during the pyrolytic process was 1,3-butadiene and that the rate constant for the reaction (2) was  $k = 1.58 \times 10^{15}$  $\exp(-62 \ k cal/RT) \ s^{-1}$  (900–1050 K). Barnard and Parrott [4] studied the thermal decomposition of 4-vinylcyclohexene between 927 and 1197 K using a single-pulse shock tube. They reported the rate constant  $k = 6.17 \times 10^{15}$  $\exp(-62.6 \ k cal/RT) \ s^{-1}$  being about four times greater than that reported by Tsang at temperatures below 1050 K. They also showed that, at higher temperatures above 1050 K, the measured rate constant fell below the extrapolation of the Arrhenius line.

The direct measurement of 1,5-cyclooctadiene and 4-vinylcyclohexene concentrations at the earlier stage in the 1,5-cyclooctadiene and 4-vinylcyclohexene pyrolysises would be more useful for a consideration of the mechanism and the rate constants at temperatures above 800 K.

In this article, we report the rate constants  $k_1, k_2$ , and  $k_3$  over the temperature range 880 K and 1230 K evaluated with a time-resolved technique.

#### Experimental

The shock tube employed in this study was described previously [6]. The time variations of 1,5-cyclooctadiene, 4-vinylcyclohexene concentrations were traced using the laser absorption apparatus described previously [7]. The transmitted intensities of a 3.39  $\mu$ m He—Ne laser beam through a 4.1 cm pathlength in the shock tube and through an interference filter  $(\lambda_{\rm max} = 3.39 \ \mu {\rm m}, {\rm half}{\rm -width} = 0.072 \ \mu {\rm m})$  were observed with Fujitsu IV-200C4 InSb detector to learn the time variation of 1,5-cyclooctadiene or 4-vinylcyclohexene. The gas compositions employed were A(2% 4)vinylcyclohexene, 98% Ar), and B (1% 4-vinylcyclohexene, 99% Ar) and C (1% 1,5-cyclooctadiene, 99% Ar). The argon (Teisan Co.) specified to be 99.999% pure was used without further purification. The 1,5-cyclooctadiene (Tokyo Kasei Co.) and 4-vinylcyclohexene (Tokyo Kasei Co.) specified to be 97% and 95% pure, respectively, were frozen, degassed a number of times and purified by trap-to-trap distillation before use. The initial pressure used was 50 torr. The computer calculations used in this study are essentially the same as described previously [8]. The thermochemical properties were computed from polynomial fits to values from literature [5].

#### **Results and Discussion**

Thermal decompositions of 1,5-cyclooctadiene and 4-vinylcyclohexene were studied over the temperature range 880–1230 K and over the pressure range 0.9–2.1 atm. Oscillograms of laser-absorption at 3.39  $\mu$ m were similar to those shown in Figure 5 of ref. [8]. At temperatures below 930 K, the absorption intensity after the schlieren-spike with the 4-vinylcyclohexene mixtures remained constant during 800  $\mu$ s. At temperatures above 930 K,

the absorption intensity after the schlieren-spike decreased with time. The rate of absorption reduction increased with increase in temperature. On the other hand, the absorption intensity after the schlieren-spike with the 1,5-cyclooctadiene mixture decreased with time even at 880 K. The rate of absorption reduction increased with increase in temperature. From the above, it can be seen that the rate of pyrolysis of 1,5-cyclooctadiene is faster than that of 4-vinylcyclohexene. The product in both the pyrolysises under our experimental conditions was analyzed with a gas-chromatograph [8]. It was confirmed that the main product was 1,3-butadiene.  $A_t$  is defined by the following equation.

$$A_t = \log(I_f/I_t)/\log(I_f/I_0)$$

where  $I_f$  is the signal voltage corresponding to the full laser intensity, and  $I_0$  and  $I_t$  are the signal voltage corresponding to the laser intensity at the reflected shock front (t = 0) and at time t, respectively. The typical timeprofiles for 1% 1,5-cyclooctadiene and 2% 4-vinylcyclohexene mixtures are shown in Figures 1 and 2, respectively. Relationships between the laserabsorption data  $A_t$  and temperature T at 50  $\mu$ s, 100  $\mu$ s, and 300  $\mu$ s for 1% 1,5-cyclooctadiene and 1% 4-vinylcyclohexene mixtures are shown in Figure 3. In order to analyze this data, the extinction coefficients for 1,3butadiene, 1,5-cyclooctadiene, and 4-vinylcyclohexene were determined as  $\varepsilon(1,3-C_4H_6) = 4.375T + 2350$ ,  $\varepsilon(cC_8H_{12}) = -36T + 81200$ ,  $\varepsilon(vC_8H_{12}) = -20T + 61000$  by using 6% 1,3-C<sub>4</sub>H<sub>6</sub>, 1%  $cC_8H_{12}$ , and 1%  $vC_8H_{12}$  mixtures diluted with argon, respectively.

To interpret this data, a computer modeling study was performed. Through trial and error methods, we attempted to find an appropriate mechanism and rate constant expressions that could predict our results. We obtained the Arrhenius equations shown in Table I over the temperature range 880-1230 K from the analysis of this data. Based upon the data scatter alone (Fig. 3), the k expressions should be accurate to within



Figure 1. Comparison of the observed time profiles  $A_t$  with the calculated ones using mixture,  $1\% cC_8 H_{12}$ , 99% Ar. ( $\triangle$ ) observed at 903 K; ( $\bigcirc$ ) observed at 993 K; ( $\square$ ) observed at 1066 K; and ( $\_\_\_$ ) calculated using Table I.



Figure 2. Comparison of the observed time profiles  $A_t$  with the calculated ones using mixture, 2%  $vC_8H_{12}$ , 98% Ar. ( $\triangle$ ) observed at 1024 K; ( $\bigcirc$ ) observed at 1125 K; ( $\Box$ ) observed at 1215 K; and ( $\longrightarrow$ ) calculated using Table I.

 $\pm 50\%$  over the temperature range studied. Systematic errors in the instrumentation may contribute this. We therefore suggest that the k expressions are probably accurate within  $\pm 70\%$ . These rate constants can predict the data shown in Figures 1–3. Comparisons of the present  $k_1$  and  $k_2$  expressions with reported ones are shown in Figures 4 and 5, respectively. The extrapolation of the Arrhenius line  $k_1$  obtained in this study shows in good agreement with those at low temperature reported by Srinivasan and Levi [1] and Doering et al. [2], as shown in Figure 4.



Figure 3. Comparison of laser-absorption data  $A_t$  observed with those calculated at 50  $\mu$ s, 100  $\mu$ s, and 300  $\mu$ s using mixtures (1%  $cC_8H_{12}$ , 99% Ar) and (1%  $vC_8H_{12}$ , 99% Ar). ( $\triangle$ ) observed using mixture (1%  $cC_8H_{12}$ , 99% Ar); ( $\bigcirc$ ) observed mixture (1%  $vC_8H_{12}$ , 99% Ar); ( $\bigcirc$ ) observed mixture (1%  $vC_8H_{12}$ , 99% Ar); ( $\bigcirc$ ) observed mixture (1%  $vC_8H_{12}$ , 99% Ar); ( $\bigcirc$ ) observed is mixture (1%  $vC_8H_{12}$ , 99% Ar) using Table I; and ( $\bigcirc$ ) calculated for mixture (1%  $vC_8H_{12}$ , 99% Ar) using Table I.

No.	Reaction	A	n	E
(1)	$cC_8H_{12} = bC_8H_{12}$	$5.2 \times 10^{14}$	0.0	48,300
(2)	$v\mathrm{C_8H_{12}} = b\mathrm{C_8H_{12}}$	$3.5 imes10^{14}$	0.0	55,300
(3)	$bC_8H_{12} = 1,3-C_4H_6 + 1,3-C_4H_6$	$1.5 imes10^{14}$	0.0	6000

TABLE I. Elementary reactions and rate constant expressions.<sup>a</sup>

<sup>a</sup> Rate constants in the form,  $AT^n \exp(-E/RT)$ , in cm, mol, cal, and K units.

Barnard and Parrott [4] showed the rate constant expression  $k_2 = 6.17 \times 10^{15} \exp(-62.6 \text{ kcal/}RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for the pyrolysis of  $vC_8H_{12}$  between 927 and 1050 K. They also showed that above 1050 K the measured rate constants fall below the extrapolation of the Arrhenius line. However, the rate constants  $k_2$  obtained from the laser-absorption profiles between 880 and 1230 K did not show the transition as reported in the single-pulse shock tube study [4]. Our rate-constant values for the pyrolysis of  $vC_8H_{12}$  are larger than those of Tsang [3] and Barnard and Parrott [4], as may be seen in Figure 5. The extrapolated values of our  $k_2$  are also larger than those estimated by Benson [5], as may be seen in Figure 5.

Using the single-pulse shock tube, both Tsang [3] and Barnard and Parrott [4] have studied the rate constant of the thermal decomposition of  $vC_8H_{12}$ . Chemical kinetic studies using the single-pulse chemical shock tubes have frequently been criticized because of uncertainties in reaction time. In an attempt to overcome the objection, a comparative technique was developed. However, there are some limitations and uncertainties for it as have mentioned by Barnard and Parrott [4]. The difference between



Figure 4. Comparison of the reported rate constants  $k_1$  with the evaluated one. (\_\_\_\_\_) this work; (\_\_\_\_\_) reported by Doering et al. [2]; and (-----) reported by Srinivasan and Levi [1].



Figure 5. Comparison of the reported rate constants  $k_2$  with the evaluated one. (\_\_\_\_\_) this work; (\_\_\_\_) reported by Barnard and Parrott [4]; (-----) reported by Tsang [3]; and (\_\_\_\_) reported by Benson [5].

our and Tsang [3] and Barnard and Parrott [4] expressions for the  $k_2$  may come from the adopted techniques.

Our data for both the pyrolysises of  $cC_8H_{12}$  and  $vC_8H_{12}$  could be explained by adopting the occurrence of a nonbranched biradical [5]. The rate constants  $k_3 = 1.5 \times 10^{14} \exp(-6.0 \ k cal/RT) \ s^{-1}$  for reaction (3), being the allylic biradical pyrolysis, were used. This value for  $k_3$  is about 10 times that estimated by Benson [5]. If Benson's expression was used for  $cC_8H_{12}$ experimental results, the calculated  $A_t$  values were much larger than the observed ones.

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